TECHNOLOGY DEPT.

Corrosion

IN THIS ISSUE:

Also: NACE News, New Products, Corrosion Abstracts

Complete Contents on Pages 2 and 3

CORROSION CONTROL
PRACTICE · INDUSTRY
NATIONAL ASSOCIATION
OF CORROSION ENGINEERS
ORGANIZED · 1943

OFFICIAL PUBLICATION
NATIONAL ASSOCIATION
of
CORROSION ENGINEERS

NOVEMBER
1959

Vol. 15 No. 11

from the makers of Dimetcote...

ZINKOTE®

THE FIRST 100% INORGANIC
SELF-CURING ZINC COATING.

- A radically new concept in zinc coatings for protecting steel.
- Under development for many years and first patented in 1957.
- Applied in one coat — completely self-curing.
- Can be used wherever galvanizing is satisfactory — actually gives superior protection.
- Completely nonflammable, nontoxic.
- Insoluble in all petroleum products.
- Outstanding resistance to weathering, salt and fresh water.
- Applied by brush, spray or roller.
- Cathodically protects steel.
- Resists temperatures up to 600°F.
- Complete protection for as little as 5¢ per square foot material cost.

For complete information write ...

How does Zinkote compare with Dimetcote? Although similar, each has certain unique advantages depending upon the particular requirements of the job. We will be glad to give you a specific recommendation.

Amercoat®
CORPORATION

Dept. GK • 4809 Firestone Boulevard • South Gate, California

| 921 Pitner Ave. | 360 Carnegie Ave. | 2404 Dennis St. | 6530 Supply Row |
| Evanston, Ill. | Kenilworth, N.J. | Jacksonville, Fla. | Houston, Texas |

The Pioneer Manufacturer of Inorganic Zinc Coatings
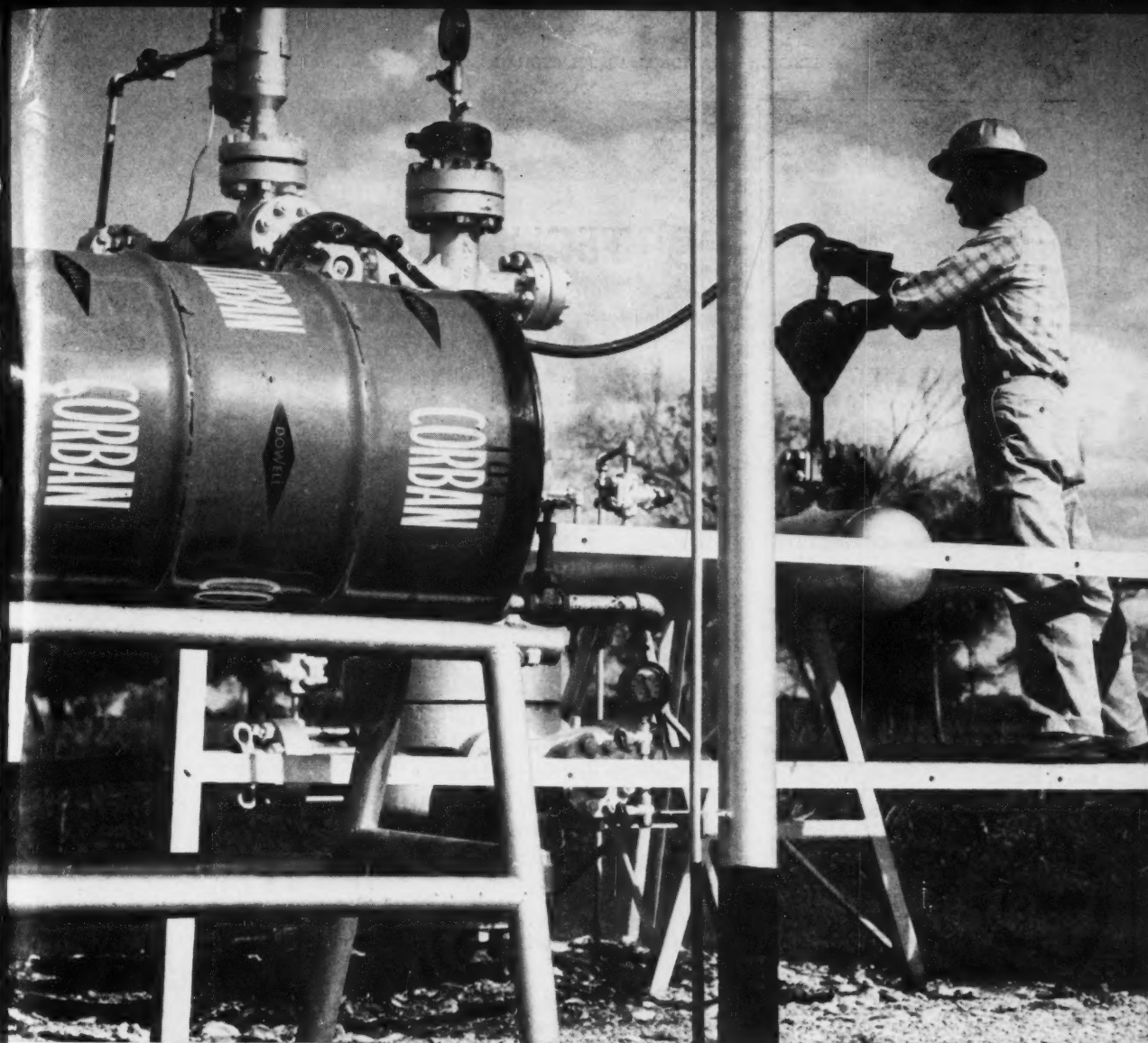
CORBAN

*17 varieties
for corrosion control;
one quality—best!*

Corban® is the name given to Dowell's family group of corrosion inhibitors. They were developed to meet *your* problems. And there is a whole family of them, because corrosive well conditions vary so much.

First, Corban is offered in three forms: "ready-to-use" liquid, concentrated liquid and sticks. Then, Corban comes in more than a dozen formulas, each one designed for sweet crude, sour crude or gas condensate wells.

Corban can be applied by three methods: simple fluid-introduction down the annulus; stick-injection through lubricators or pressure locks; and the "squeeze" method of pumping liquid Corban back into the producing formation—proved for corrosion control over extended periods of time.

A variety of forms and formulas—to meet and control any corrosion problem on any well—is yours when you specify Corban. And, despite this variety, Corban is consistent in *quality*. Ask for an engineered corrosion study and recommendation from any of the 165 Dowell service points and offices. Dowell serves the oil industry in the United States, Canada, Venezuela and Argentina. Dowell, Tulsa 1, Oklahoma.

Products for the oil industry ◆ DOWELL
DIVISION OF THE DOW CHEMICAL COMPANY

CONTENTS

TECHNICAL SECTION

Technical Topics to Be Indexed in December Issue

Technical Topics published in CORROSION will be included in the alphabetical subject index, accumulated contents and their authors listed in the alphabetical author index which will appear in the December issue.

CONTENTS

TECHNICAL COMMITTEE ACTIVITIES

NACE NEWS

TECHNICAL TOPICS

GENERAL NEWS

NACE Corporate Members and Representatives

Administracion Nacional de Combustibles
Alcohol y Portland,
Ing. Esequiel Perez Prins
Alabama Gas Corporation
T. G. Humphreys, Jr.
Allegheny Ludlum Steel Corp.
William G. Renshaw
Allied Chemical Corp.,
Plastics & Coal Chemicals Div.
P. B. Mayfield
Allied Chemical Corp., General Chemical
Div.
W. H. Burton
Allied Chemical Corp., Solvay Process Div.
G. E. Best
Allied Chemical Corp., Nitrogen Division
H. C. Wintzer
Alloy Steel Products Co.
R. M. Davis
Aluminium Laboratories, Ltd.
H. P. Godard
Aluminum Company of America
Ellis D. Verink, Jr.
Amchem Products, Inc.
Alfred Douty
Amercoat Corp.
C. G. Munger
American Brass Co., The
John R. Freeman, Jr.
American Mollerizing Corp.
H. E. Linden
American Oil Company
Walter S. Janssen
American Smelting Refg. Co., Federated
Metals Div.
R. D. Taylor
American Telephone & Telegraph Co.
A. F. Minor
American Tobacco Co., The
A. R. Anderson
American Zinc, Lead & Smelting Co.
Robert Ammon
Apex Smelting Co.
A. J. Peterson
Aquatrol, Inc.
M. C. Forbes
Arabian American Oil Co.
William F. Gross
Arizona Public Service Co.
Frank Buck
Arkansas Fuel Oil Corp.
L. F. Babcock
Arkansas Louisiana Gas Co.
W. A. Broome
Armco Steel Corp.
Arba Thomas
Armour Chemical Division, Armour & Co.
J. E. Maloney
Atchison, Topeka & Santa Fe Railway
Co., The
E. B. Fields
Atlantic Pipe Line Co. (Penna.) Product
Pipe Line Dept.
Robert H. Lynch
Atlantic Refining Co., Producing Div.,
The
V. E. Stepp
Atlantic Refg. Co., Refining Div., The
J. K. Delchler
Atlas Mineral Products Co., The
Joseph A. Snook
Atlas Powder Company, Aquaness
Department
Fritz E. Fuchs

Babcock & Wilcox Co., The
F. Eberle
Baltimore Gas & Electric Co.
T. J. Dwyer
Baltimore & Ohio RR Co., The
K. K. Kessler
Barnes & Delaney
Pipe-Coating
William R. Houck
Barnup and Sims, Inc.
James H. Graham
Bataafsche Petroleum Mij., N. V. de
H. A. van Offeren
Bechtel Corporation
G. B. Grable
Bell Telephone Lab.
Vernon B. Pike
Bessemer & Lake Erie Railroad Co.
R. D. Lake
Bethlehem Steel Co.
Seymour Charles Frye
Betz Laboratories, Inc.
W. A. Tanzola
Bird-Archer Co., The
Charles W. Bird
Blaw Knox Co., Chemical Plants Div.
John Kull
Brance-Krachy Co., Inc.
Wayne E. Broyles
Bridgeport Brass Co.
R. V. Hall
Briggs Bituminous Composition Co.
J. D. Farber
Briner Paint Mfg. Co., Inc.
Felix Kelinske
British American Oil Co., Ltd.
L. P. Blaser
BP (North America) Limited
T. E. Pitkethly

Byers Co., A. M.
R. J. Bricmont
California Research Corporation
F. W. Schremp
Cameron Iron Works, Inc.
Rudy Zorn
Canadian Protective Coating Ltd.
F. W. Hewes
Canadian Vickers Limited
P. W. Gooch
Canadian Western Natural Gas Co., Ltd.
G. D. Kellam
Cathodic Protection Service
E. P. Doremus
Cellcote Co., Inc., The
R. E. McMahon
Celanese Corp. of America
J. A. Manning
Central Power & Light Co.
William M. Mayer
Chain Belt Co. of Milwaukee
Egmont R. Helmer
Champion Paper & Fibre Co., The
Peter A. Kimen
Champlin Oil & Refining Co.
K. C. Cribley
Chanslor-Western Oil & Dev. Co., Chans-
lor-Canfield Midway Div.
John L. Stephens
Chesapeake and Ohio Railway Company,
The, C. M. Angel
Chicago Bridge & Iron Co.
I. E. Boberg
Cincinnati Gas & Electric Co., The
Milton J. Pfeiffer
Cit-Con Oil Corp.
Robert L. Hale, Jr
Cities Service Gas Co.
Clint D. Rogers
Cities Service Pipe Line Co.
Harry Nelson
Cities Service Refining Corp.
L. D. Mann
Clementina, Ltd.
K. F. Keefe
Clemtex, Ltd.
Frank E. Wilson
Coast Paint & Lacquer Co., Inc.
R. M. Johnson
Colorado Interstate Gas Co.
Preston Parks
Columbia Gas System Service Corp.
J. E. Overbeck
Columbia-Southern Chemical Corp.
G. Heinemann
Columbus & Southern Ohio Electric Co.
N. R. Patton
Commercial Solvents Corporation
Richard S. Egly
Commonwealth Associates Inc.
W. E. Bunting
Commonwealth Edison Co.
Earle Wild
Consolidated Edison Co. of New York,
Inc.
L. B. Donovan
Consolidated Mining & Smelting Co. of
Canada, Ltd.
J. R. Wellington
Consumers Power Co.
J. B. Simpson
Continental-Emsco Co.
Albert S. Holbert
Continental Pipe Line Co.
I. E. Maddux
Cook Paint & Varnish Co.
Decker Freeman
Cooper Alloy Corp.
Herbert J. Cooper
Corn Prod. Co.
Technical Div.
R. E. Pierson
Corrosion Rectifying Co.
Wayne A. Johnson
Cosden Petroleum Corp.
R. W. Thompson
Crane Co.
Chester Anderson
Creole Petroleum Corp.
S. J. Mathis
Crown Central Petroleum Corp.
A. J. Morris
Crutcher-Rolfs-Cummings, Inc.
Jack Scott
Syd E. Culbertson Co., Inc.
William B. Schell

Dallas Power & Light Co.
Robert D. Elliott
Dampney Co., The
J. Dwight Bird
Day, S. D., Co.
David W. Peaks
The Dayton Power & Light Co.,
Corrosion Control Dept.
Paul C. Hoy
Dearborn Chemical Co.,
R. F. Carr, Jr.
Deberoise Co., The
Robert L. Deberoise
Delhi-Taylor Oil Corp.
Walter E. Anderson
De Vilbiss Co., The
D. J. Peeps
Diamond Alkali Company
S. W. McIlrath
Douglas Aircraft Co., Inc.
F. T. Wood, Jr.

Dow Chemical Co., The
H. A. Humble
Dowell
Guy F. Williams
E. I. du Pont de Nemours & Co., Inc.
J. A. Collins
Duriron Co., The
W. A. Luce
Duval Sulphur & Potash Co.
J. W. Borskey, Jr.

East Bay Municipal Utility District
Lee B. Hertzberg
Eastern States Petroleum & Chem. Corp.
Jack Dalberg
Ebasco Services, Inc.
Electro Rust-Proofing Corp.
Frank P. Macdonald
Elizabethtown Consolidated Gas Co.
George H. Coon
El Paso Natural Gas Co.
L. G. Wainman
Esso Research & Engineering Co.,
Design Div., M. S. Northup
Ethyl Corp.
H. S. Butler

Fabri-Valve Co. of America
J. L. Williams
Farboil Co.
Irvin Baker
Fibreboard Paper Products Corp.
Pabco Indus. Insulations Div.
L. S. Parker
Food Machinery & Chemical Corp.
Central Engineering Labs.
E. H. Brink
Frances Oil Co.
Frances Olsan
Freeport Sulphur Co.
William J. Blanchard
Furane Plastics Inc.
John Delmonte

F. W. Gartner Company
F. W. Gartner, Jr.
General American Transportation Corp.
Paul Talmey
General Electric Co., Industrial Mate-
rials Div., H. A. Cataldi
General Petroleum Corp.
Ralph M. Willits
Gibbs & Hill, Inc.
E. H. Anson
Good-All Electric Mfg. Co.
Troy R. Stilley
B. F. Goodrich Chemical Co.
R. J. Collins
Graver Tank & Mfg. Co., Inc.
Phillip E. Rose
Great Lakes Pipe Line Co.
C. C. Keane
Great Northern Railway Co.
G. V. Guerin
Gulf Oil Corp.
Walter F. Rogers
Gulf Oil Corp., Mfg. Div.
D. L. Burns
Gulf Research & Development Co.
L. W. Vollmer
Gulf States Utilities Co.
W. W. Eckles
Gunnels Co., W. D.
Wm. H. Stemler

Hackensack Water Co.
A. Damiano
Hagan Chemicals & Controls, Inc.
Threshold Treatment Div.
John P. Kleber
Halliburton Oil Well Cementing Co.
Roy Stout
Harbison-Fischer Manufacturing Co.
D. T. Harbison
Hercules Powder Co., Chemical Eng. Div.
David J. Torrans
Hill, Hubbell & Company,
Division of General Paint Corp.
Milton M. Bowen
Holcombe Company, Inc., The
Tom L. Holcombe
Holders Equipment Co.
S. D. McMullen
Hooker Electrochemical Co.
Walter A. Szymanski
Houston Contracting Co.
R. P. Gregory
Houston Natural Gas Corp.
W. C. Dahlman
Houston Pipe Line Co.
H. D. Carmouche
Humble Oil & Refining Co.
H. D. Wilde
Humble Pipe Line Co.
A. E. Pecore
Hydro-Electric Power Commission of
Ontario, The
D. G Watt

Imperial Oil, Ltd., Pipe Line Division
B. H. Mackenzie
Imperial Oil, Ltd., Prod. Dept.,
Western Div.
J. W. Young
Imperial Pipe Line Co., Ltd., The
E. W. Christian
Inland Steel Co., Indiana Harbor Works
R. L. Harbaugh
Instituto Venezolano de Petroquimica
Mario Oliver A.
International Harvester Co.
Earl F. Moorman
International Nickel Co., Inc., The
W. Z. Friend
International Nickel Co. of Canada,
Ltd., The
R. J. Law
International Paint Co., Inc.
Albert R. Smiles
International Rectifier Corp.
F. W. Parrish
Interprovincial Pipe Line Co.
F. J. Stubbs
Iowa Public Service Co.
Wm. J. Dougherty
I.A.R.M., H. O. Operations

Jersey Production Research Co.
S. P. Ewing
Johns-Manville Corp.
M. W. Gregory
Jones-Blair Paint Co.
L. R. Kyrias
Jones & Laughlin Steel Corp.
H. T. Clark

Kansas-Nebraska Natural Gas Co., Inc.
Leonard C. Hill
M. W. Kellogg Co., The
W. B. Hoyt
Kendall Co., The, Polyken Sales
Division, Howard D. Segool
Keystone Roofing Manufacturing Co.
Stephen A. Feely
Keystone Shipping Co.
S. F. Spencer
Koppers Co., Inc., Tar Prod. Div.
W. F. Fair, Jr.
Kraloy Plastic Pipe Co., Inc.
Russell W. Johnson

Laclede Gas Co.
Delmar Hasenritter
Lester Equip. Manuf. Co., Inc.
Don P. Wilson
Lever Brothers Co.
E. K. Holt
Lion Oil Co.
J. B. Rogerson
Lone Star Gas Co.
John M. Kindle
Long Island Lighting Co.
William Welch, Jr.
Lubrizol Corp., The
Willis G. Craig

Magnolia Petroleum Co.
J. D. Humble
Magnolia Pipe Line Co.
James R. Ashley
Mallinckrodt Chemical Works
C. A. Coberly
F. H. Maloney Co.
James H. McBrien
Manning, Maxwell & Moore, Inc.
Robert F. Ehrsam
Mavor-Kelly Company
Thos. F. P. Kelly
Metal Goods Corp.
Charles G. Gribble, Jr.
Metallizing Engineering Co.
R. J. McWaters
Metropolitan Water District of So. Calif.
R. B. Diemer
Michigan Consolidated Gas Co.
Karl E. Schmidt
Mid-Continent Pipe Line Co.
F. E. Pyeatt, Jr.
Mid-Valley Pipeline Co.
F. H. Deal
Midwestern Pipe Line Products Co.
John R. Wilson
Minnesota Mining & Mfg. Co.
W. C. O'Leary
Mississippi River Fuel Corp.
G. B. Lowther
Mississippi Valley Gas Co.
J. H. Lambdin
Moncrief Lenoir Mfg. Co.
Mrs. Peuny H. Williams
Monsanto Chemical Co.
F. L. Whitney, Jr.
Montana Power Co.
Carl R. Davis
Morton Salt Company
Horace W. Diamond
Mountain Fuel Supply Co.
Harry R. Brough
Napko Corp.
Joseph E. Rench
Nalco Chemical Company
J. W. Ryznar

NACE Corporate Members and Representatives

National Lead Co.
  Roy Dahlstrom
National Steel Corp.
  Res. & Dev. Dept.
  E. J. Smith
National Supply Co., Tubular Div.
  Dr. Lawrence E. Trishman
National Tank Co.
  Clarence O. Glasgow
Natson Mfg. Co.
  Anil N. Shah
New Jersey Zinc Co. of Pa., The,
  Research Dept.
  E. A. Anderson
New Orleans Public Service, Inc.
  Lionel J. Cucullu
Nicolet Industries, Inc.
  Ladd L. Wilson
Norfolk & Western Railway Co.
  C. L. Crockett
Northern Illinois Gas Co.
  M. G. Markle
Northwestern Utilities, Ltd.,
  M. E. Stewart

Oakite Products, Inc.
  Robert F. Ayres
Ohio Oil Co., The
  Ralph M. Slough
Oil Well Supply Div.
  F. L. Current
Oklahoma Natural Gas Co.
  P. K. Wallace
Olin Gas Transmission Corp.
  O. C. Roddey
Olin Mathieson Chemical Corp., Tech.
  Div., Metals
  John B. Seastone
Omaha & Council Bluffs Electrolysis
  Committee
  R. A. Pesek
Otis Engineering Corp.
  W. M. Kelly
Owens-Corning Fiberglas Corp.
  William A. Stutts

Pacific Gas & Elec. Co.
  Roy O. Dean
Pacific Lighting Gas Supply Co.
  N. K. Senatoroff
Pacific Northwest Pipeline Corp.
  William C. Brady
Page-Hersey Tubes, Ltd.
  John D. Breithaupt
Pan American Petroleum Corp.
  Joseph B. Clark
Panhandle-Eastern Pipe Line Co.
  M. K. Hager
Parker Rust Proof Co.
  E. W. Richards
Pennsalt Chemicals Corp.
  R. R. Pierce
The Pennsylvania Railroad Co.
  M. A. Pinney
Peoples Gas Light & Coke Co., The
  J. L. Adkins
Permian Enterprises, Inc.
  Thomas H. Duff
Perrault Equipment Co.
  V. V. Malcom
Petrolite Corp.
  G. J. Samuelson
Philadelphia Electric Co.
  E. S. Halfmann
Philip Carey Manufacturing Co., The
  John F. MacKay
Phillips Petroleum Co.
  Frederick A. Prange
Pipe Line Service Corp.
  F. C. Yeazel
Pipe Linings, Inc.
  Robert L. Hansen
Pittsburgh Coke & Chemical Co.
  A. E. Gray
Plantation Pipe Line Co.
  W. G. Horstman
Plastic Applicators, Inc.
  H. M. Kellogg
Plastic Engineering & Sales Corp.
  Sam D. Hollinger
Plicoflex, Inc.
  B. E. Black
Portland Pipe Line Corporation
  Carlton L. Goodwin

Premier Oil Refining Co. of Texas
  David D. Pickrell
H. C. Price Co.
  R. P. White
Procter & Gamble Co., Engr. Div., The
  George F. Lockeman
Production Profits, Inc.
  H. L. Bilhartz
Products Research Service, Inc.
  Philip B. Wogan
Public Service Electric & Gas Co.
  Donald C. Luce
Pure Transportation Co.
  D. C. Glass

Radio Receptor Company, Inc.
  Julian Loebenstein
Raytherm Corporation
  F. Raymond Young
Reilly Tar & Chemical Corp.
  J. H. Barnett, Jr.
Republic Steel Corp.
  Giles Locke
Reynolds Metals Company
  Robert S. Dalrymple
Cyrus Wm. Rice & Co.
  James K. Rice
Richfield Oil Corp.
  D. F. Purdy
Robinson, E. W. Supply Co.
  James E. Freeman
Rochester Gas & Electric Corp.
  Edward J. Nelson
Rockwell Mfg. Co., Meter & Valve Div.
  Jack W. Harris
Rosson-Richards Co.
  S. L. Richards, Jr.
Rust Proofing, Inc.
  Harold B. Newsom

S.T.E.C.T.A.
  Georges Poirier
St. Joseph Lead Co.
  Dwight Marshall
St. Louis Metallizing Co.
  Walter B. Meyer
St. Louis-San Francisco Railway Co.
  M. A. Herzog
Salt Lake Pipe Line Co.
  L. G. Haskell
San Diego Gas & Electric Co.
  Donald P. Armbruster
San Francisco Water Dept.
  James H. Turner
Sargent & Lundy
  Ludwig Skog, Jr.
IMPER—Ing. A. Schieroni & Figli
  Ing. Franco Schieroni
Service Pipe Line Co.
  J. R. Polston
Shamrock Oil & Gas Corp., The
  Dan P. Long
Shawinigan Resins Corporation
  Karl K. Mahaffey
Shell Chemical Corp.
  A. L. Petersen
Shell Development Co.
  R. S. Treseder
Shell Oil Co., Inc.
  W. A. Bonner
Shell Pipe Line Corp.
  L. B. Nelson
Shippers' Car Line Division ACF Industries
  Ernest H. Colby
Signal Oil & Gas Co.
  E. O. Kartinen
Sinclair Pipe Line Co.
  Glenn L. Ladd
Sinclair Research Laboratories, Inc.
  F. M. Watkins
Sline Industrial Painters
  Louis L. Sline
A. O. Smith Corp.
  L. C. Wasson
Socony Mobil Oil Co. Inc.,
  Central Pipe Lines Div.
  Gerald J. Paisley

Socony Mobil Oil Co. Inc.,
  Eastern P. L. Div.
  S Kleinheksel
Socony Paint Products Co.
  Edwin Saul, Jr.
Sohio Petroleum Co.
  S. B. Lisle
Sohio Pipe Line Co.
  A. A. Dorffi
Southeastern Pipe Line Co.
  R. P. Hamilton
Southern Bell Telephone & Telegraph Co.
  T. J. Cook
Southern California Gas Co.
  J. S. Dorsey
Southern Counties Gas Co. of Calif.
  W. C. Mosteller
Southern Minerals Corp.
  F. P. Peterson, Jr.
Southern Natural Gas Company
  O. W. Clark
Southern Pacific Company
  W. M. Jaekle
Southern Pacific Pipe Lines, Inc.
  W. T. Eskew, Jr.
Southern Union Gas Co.
  N. P. Chesnutt
Southwest Natural Gas Co.
  F. A. Merfeld
Southwestern Electric Power Co.
  J. E. Moody
Southwestern Public Service Co.
  H. O. Hodson
Spencer Chemical Company
  Ralph D. Miller
Stainless Foundry & Engineering, Inc.
  Thomas E. Johnson
Standard Oil Co. of Calif.
  D. Roger Loper
Standard Oil Co. (Ind.),
  Pro. Pipe Line Dept.
  V. M. Kalhauge
Standard Pipeprotection, Inc.
  Hugh W. Baird
Standard Railway Equipment Mfg. Co.
  J. S. Swann
Stauffer Chemical Co.
  J. B. Ceccon
D. E. Stearns Co., The
  D. E. Stearns
Steelcote Manufacturing Co.
  Douglas A. Niedt
Sun Oil Co. Production Laboratory
  William F. Oxford
Sun Pipe Line Co.
  W. H. Stewart
Sunray Oil Corp.
  John Stone
Superior Iron Wks. & Sply. Co., Inc.
  V. J. Martzell
Superior Oil Company, The
  William H. Edwards

Tennessee Gas Transmission Co.
  J. L. Parrish, Jr.
Texaco-Cities Service Pipe Line Co.
  B. W. Nedbalek
Texaco, Inc.
  W. S. Quimby
Texas Eastern Transmission Corp.
  Pat H. Miller
Texas Electric Service Co.
  C. W. Geue
Texas Gas Transmission Corp.
  Fred D. Stull
Texas Gulf Sulphur Co.
  C. O. Stephens
Texas Pipe Line Co., The
  Paul T. Miller
Texsteam Corporation
  L. V. Musgrove
Tex-Tube, Inc.
  R. W. Kearney
Thornhill-Craver Co.
  C. R. Horn
Tidewater Oil Co.
  A. M. Mouser

Tinker & Rasor
  Leo H. Tinker
Trans-Arabian Pipe Line Co.
  P. P. Nibley

Transcontinental Gas Pipe Line Corp.
  S. J. Bellassai
Trans Mountain Oil Pipe Line Co.
  C. D. Bailey
Trans-Northern Pipe Line Co.
  L. R. Dickinson
Tresco, Inc.
  D. L. Korn
Triangle Conduit & Cable Co., Inc.
  Roger E. Martin
Trunkline Gas Co.
  A. T. Surber, Jr.
Truscon Labs Div.
  Devoe & Raynolds Co., Inc.
  R. E. Madison
Tube-Kote, Inc.
  E. G. Holm
Tube Turns Plastics, Inc.
  George H. Hunt
Tuscarora Pipe Line Company, Ltd.
  John W. de Grott

Union Carbide Corp.
  George A. Sands
Union Electric Co.
  George P. Gamble
Union Gas Company of Canada, Ltd.
  Ralph E. Kuster
Union Oil Co. of Calif., Research Center
  J. E. Sherborne
Union Pacific Railroad Co.
  Lee S. Osborne
Union Producing Co.
  E. L. Rawlins
Union Tank Car Co.
  Daniel W. Havens
United Gas Corp.
  C. L. Morgan
United Gas Pipe Line Co.
  M. V. Cousins
United States Pipe & Foundry Co.
  A. E. Schuh
U. S. Steel Corp., National Tube Div.
  Raymond C. Bowden, Jr.
United States Steel Corp., Applied
  Research Laboratory
  C. P. Larrabee
Universal Control Corp.
  Charles D. Peterson
Universal Oil Products Co.
  Eugene M. Matson

Vapor Honing Co., Inc.
  Jack Eggleston
Vapor Recovery Systems Co.
  Frank V. Long, Sr.
Visco Products Co., Inc.
  D. M. Jacks

Western Kentucky Gas Co.
  J. L. Bugg
Western Natural Gas Co.
  Paul C. Wright, Jr.
Wheeling Steel Corporation
  Henry A. Stobbs
T. D. Williamson, Inc.
  T. D. Williamson, Jr.
Wisconsin Protective Coating Co.
  Francis J. Ploederl
Wolverine Tube Division of
  Calumet & Hecla, Inc.
  John M. Keyes
Worthington Corp.
  W. M. Spear
Wright Chemical Corp.
  Paul G. Bird
Wyandotte Chem. Corp.
  L. W. Gleekman

Youngstown Sheet & Tube Co., The
  Karl L. Fetters

SCHEDULED FOR PUBLICATION IN DECEMBER CORROSION

CORROSION's annual index of technical articles and Technical Topics published during 1959 will appear in the December issue.

• • •

An Industrial Experience of Attack on Metals by Synthesis Gas From Methane-Oxygen Combustion, by F. Eberle and R. D. Wylie

High Temperature Metal Deterioration in Atmospheres Containing Carbon-Monoxide and Hydrogen, by W. B. Hoyt and R. H. Caughey

Corrosion of Metals at Mandapam Camp, India, by K. S. Rajagopalan, M. Sundaram and P. L. Annamalai

Case Histories and Ratings vs Corrosives of Polyester Fiber Glas Equipment, by Robert E. Barnett and Thomas F. Anderson

Corrosion in a Hydrocarbon Conversion System, by F. A. Prange

In 1954, a survey of the 6,000 odd wells in the Hugoton Gas Field revealed 56 leaks. Since most of the wells were comparatively new (two-thirds were less than five years old), this was a serious problem. Projecting the rate of leak increase showed there would be over 300 leaks by 1960.

The cost of repairing these production wasting leaks usually ran between $10,000 and $40,000, using liners or the cement squeeze method. Several Hugoton producers decided to take immediate preventative action. After extensive field tests were made, it appeared that sulfate-reducing bacteria was the villain. These microorganisms convert the sulfates into hydrogen sulphide, which in turn attacks the casings. A Dow mag-

nesium anode distributor was asked to make an analysis of the situation and recommend a practical solution.

In determining the most practical type of corrosion protection, two factors had to be considered. First, the wells were situated a mile apart and few electric power lines were available. This meant a considerable expense if cathodic equipment requiring a power source were used. Second, to what depth would protection be possible? In some soil conditions, cathodic protection cannot be used at all. In the Williston Basin, for example, a massive layer of salt above the corroding formation blocks electrical currents from reaching this portion of the casing. Fortunately, the Hugoton field was free and clear of such obstructions.

By running potential-drop tests in casings throughout the field, it was found that a current of from 0.5 to 2.5 am-

MAGNESIUM ANODES in a wide range of sizes and shapes provide flexibility to allow the most efficient design in many different types of installations. Galvomag anodes (shown above) have 25% more throwing power than ordinary magnesium anodes . . . are used extensively in the Hugoton Field.

DOW DISTRIBUTORS provide experienced technical services on corrosion problems. Field tests of soil conditions and analyses of the requirements of individual wells can result in substantial savings in installation and anode costs.

peres would provide ample protection to total depth. The installation of Galvomag® magnesium anodes was recommended as the best solution, from the standpoint of economy, as well as ease of installation. Also, as magnesium anodes do not set up "stray" currents in the soil, there was no danger of interference with foreign structures.

Three to eighteen anodes were used per well, at a total cost of from $150 to $500 per installation. A maximum of seven were used in each bed, about 85-100 feet away from the casing. Each well was examined individually to determine the most efficient installation. Factors such as variation in soil resistance, well-to-earth resistance and potential, and current requirements were

taken into full account in selecting the number and arrangement of anodes to be used for each well. The installations were designed for a ten year life but they may last 15 to 18 years because of polarization of the well casings.

Since 1954, over 800 wells in the Hugoton Gas Field have been cathodically protected with magnesium anodes. Casing leaks due to external corrosion are no longer a problem on these wells.

The Dow magnesium anode distributors listed below are ready to help you get the most for your corrosion protection dollar. Contact one of them next time you have a corrosion problem involving well casings, pipelines, storage tanks or other equipment.

AU-9

CALL THE DISTRIBUTOR NEAREST YOU:

CATHODIC PROTECTION SERVICE, Houston, Texas
CORROSION SERVICES, INC., Tulsa, Oklahoma
ELECTRO RUST-PROOFING CORP. (Service Division), Belleville, N. J.
ETS-HOKIN & GALVAN, San Francisco, Calif.
THE HARCO CORP., Cleveland, Ohio
INTERPROVINCIAL CORROSION CONTROL COMPANY, Burlington, Ontario
ROYSTON LABORATORIES, INC., Blawnox, Penna.
STUART STEEL PROTECTION CORP., Plainfield, N. J.
THE VANODE CO., Pasadena, Calif.

THE DOW CHEMICAL COMPANY · MIDLAND, MICHIGAN

Controlling Internal Corrosion of Tank Ships*

By J. FRANKLIN KOEHLER

Abstract

Some of the measures taken by Esso Standard Oil Company to control internal corrosion in its tankers are described. These include partial and complete cathodic protection, inhibition, coatings and combinations of these methods. Some of the economics of the various control measures are discussed and tabulated.

Coatings currently are considered to offer the best promise of adequate control at lowest costs. Experience with coatings on Esso tankers is related. Relative advantages and disadvantages of and the economic aspects of the available control measures are considered.   8.9.5

CORROSION of internal tank structure of vessels operating in clean/specialty service has proved to be expensive. Even the localized pitting-type corrosion common to dirty service operations is costing far more than previously estimated. Recent reconditioning repairs carried out on a number of T-2 type vessels has emphasized the increasing magnitude of corrosion losses. For example, the cost of carrying out required reconditioning repairs to the cargo tank structure of sixteen T-2 size vessels in the Esso Fleet has averaged $73,000 per vessel per year of clean service. Replacement of bottom-shell plating due to pitting-type corrosion has cost an average of $29,000 per vessel per year of dirty service. These costs are for structural replacements alone and exclude charges for such other items as interim structural repairs (voyage or annual repair periods), tank cleaning/gas freeing and rust removal costs, pipeline, valve and pump repairs, initial cost and revenue-loss resulting from oversize scantlings, etc.—which are all directly attributable to corrosion in cargo compartments. These additional costs can easily boost the total average cost of corrosion to $150,000 or more per year of clean service for T-2 size vessels. The annual cost for cargo tank corrosion in large tanker fleets therefore can amount to many hundreds of thousands of dollars.

Previous Methods of Corrosion Control

During the past seven years a joint Esso Standard Oil Company/Esso Research and Engineering Company Laboratory and shipboard testing program has been carried out to find a practical solution to the clean service corrosion problem. Many possible solutions to this problem, including the use of improved low-alloy steels, cathodic protection, inhibitors (both oil and water soluble) dehumidified air, coatings, etc., have been investigated. As a result of the ex-

* Submitted for publication January 12, 1959. A paper presented under the title "Developments in Controlling Cargo Tank Corrosion," at the 15th Annual Conference, National Association of Corrosion Engineers, Chicago, Ill., March 16-20, 1959.

perience with early experimental shipboard systems, chemical inhibitor spray and cathodic protection corrosion control systems were developed for practical full-scale application to 16,000 DWT size vessels in 1955. Since then four Esso Standard Oil Company vessels have been fitted with full-scale magnesium anode systems,[1] six vessels with full-scale combination magnesium anode/inhibitor spray systems[2] and four other vessels with partial cathodic protection systems. These protection systems have been in operation for three to four years. Actual installation, maintenance and operating costs of the full-scale systems have confirmed preliminary estimates that it will cost approximately $280,000 per vessel for these systems over a ten-year period.

Effectiveness of Previous Methods

Effectiveness of these full-scale anode and anode/inhibitor spray systems in controlling corrosion on clean-service vessels has been determined by two principal methods: 1. By comparing the measured corrosion rates on corresponding structure of the protected and non-protected vessels. 2. By comparing the over-all structural condition of the protected and non-protected vessels at corresponding clean-service life periods. These methods of evaluation, based on thousands of ultrasonic thickness measurements, confirm earlier estimates of the effectiveness of these systems and are illustrated in Figures 3, 4 and 5.

Figure 3 graphically compares the current and estimated future structural condition of three fully protected vessels[3] with the estimated structural condition[4]

(1) Anodes installed in all cargo tanks; vessel follows a "rotated ballast schelude" so that every cargo tank is ballasted at least one out of every two consecutive voyages. See Figure 1.
(2) Anodes installed in regular ballast tanks, chemical inhibitor spray system permanently installed in all non-ballast tanks. See Figure 2.
(3) These vessels are fitted with full-scale anode/inhibitor spray systems which have been in operation since these vessels entered clean service.
(4) The Structural Ratings of the non-protected vessels at the time of reconditioning vary considerably, and reflect the influence of (a) the tanker market, (b) future service (clean or dirty) for each vessel, (c) shipyard repair cost level etc. in determining the extent and time of reconditioning each particular vessel.

J. FRANKLIN KOEHLER is a member of the Repair Division of the Esso Standard Oil Company Marine Department, New York City. His work involves corrosion control methods for cargo tankers.

of ten non-protected reconditioned vessels at the time of reconditioning. This graph shows that during the five to seven-year clean service period when the non-protected vessels had to be reconditioned, the three protected ships are structurally considerably better. The structural condition of the protected vessels is sufficiently good after seven years of clean service to make the normally required reconditioning repairs unnecessary. The vessels can also be maintained in clean service beyond seven years for an additional period—still without reconditioning being required.

Figures 4 and 5 illustrate the average percent reduction in the corrosion rate being obtained with the present full-scale protection systems. As shown in these figures, approximately 50 percent reduction in the corrosion rate is being achieved
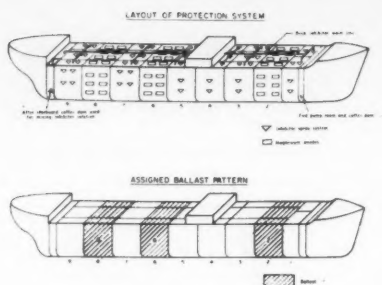
Figure 1—The combination magnesium anode/inhibitor spray system includes the use of sacrificial magnesium anodes for protection of regular ballast tanks and an inhibitor spray (applied through a fixed spray system) for protection of the remaining (non-ballast) tanks. Together these systems provide protection against corrosion to all cargo compartments of the vessel. The vessel follows a fixed ballast pattern when under protection by the combination system. Shown below is a typical arrangement of this system, with the assigned ballast pattern, for application to T-2 type vessels.

Figure 2—The full-scale cathodic protection system includes the use of sacrificial magnesium anodes for protection of all cargo tanks of the vessel. To protect all of the internal tank body it is necessary that the vessel follow a "rotated" system of ballasting whereby every cargo tank is ballasted at least one out of every two voyages. Typical ballast patterns used in the "rotated" system for a T-2 type vessel are shown.
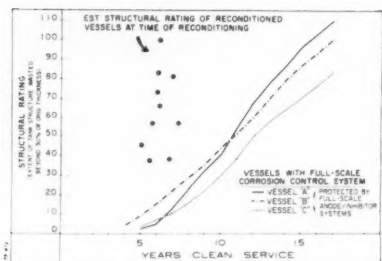
Figure 3—Comparison of structural rating, protected and non-protected vessels.

on transverse and longitudinal bulkhead structure. The vessels fitted with the combination anode/spray systems generally are protected to a greater degree than those vessels fitted with full-scale magnesium anode systems.

These figures confirm that a substantial reduction in internal corrosion is being provided by the existing protection systems.

New Developments—Coatings

Most Promising Method

Application of coatings to internal tank structures has become one of the most promising methods of controlling cargo tank corrosion under both clean and dirty service conditions. The recent and continuing development of more durable paints and specialized shipyard
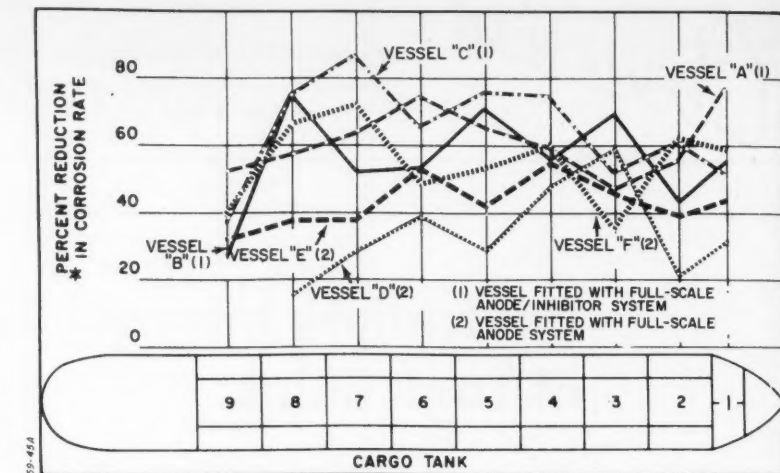
* BASED ON COMPARISON OF AUDIGAGE DATA FROM PROTECTED AND NON-PROTECTED VESSELS

Figure 4—Reduction in corrosion rate—longitudinal bulkheads, clean service vessels with full-scale protection systems.
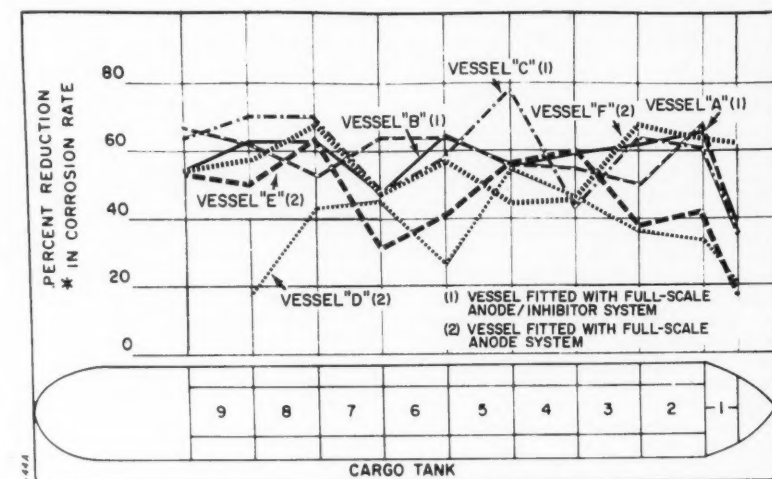
* BASED ON COMPARISON OF AUDIGAGE DATA FROM PROTECTED AND NON-PROTECTED VESSELS

Figure 5—Reduction in corrosion rate—transverse bulkheads, clean service vessels with full-scale protection systems.

application procedures is making the use of coatings in tanker cargo compartments increasingly attractive.

In 1956 seven cargo tanks on two Esso Standard Oil Company clean/specialty service vessels were completely coated for corrosion control purposes. Inspection of these coated compartments after 36 months of service has confirmed that the coating system is an effective and desirable method of corrosion control. Based on present experience, a 10-year life for these initial coating applications appears to be both possible and realistic.

A wide variety of coatings is available today for use in cargo compartments. Vinyl, epoxy, inorganic metal-pigmented type paints, etc., are being investigated for tanker service. However, only a few coatings, selected from hun-

dreds of different materials now available, actually have been applied to cargo tank structure. Even fewer coatings have been in service for any appreciable time. An inorganic zinc-pigmented coating is one of the coating materials giving satisfactory service after a number of years in clean-products trade. Because of its proved service characteristics, this type of material was selected for coating complete cargo compartments on Esso vessels —and has been applied already to over 60 cargo tanks. While this coating is proving very satisfactory, other coating materials are continually being screened and tested in an effort to find the most desirable coating from the standpoint of application requirements, cost, life and service characteristics. Small-scale shipboard tests (about 1000 square feet per coating) are underway on several tankers

to obtain actual operating experience with various types of materials.

Coating vs Anodes

The use of full-scale coating, magnesium anode or combination magnesium anode/coating systems[5] is considered to be the most practical answer to the cargo tank corrosion problem for larger tankers which are now being assigned to multigrade clean service. Comparative costs, as well as particular advantages and disadvantages, of each of these systems have been carefully investigated.

Based on past experience, installation/application and maintenance costs have been estimated for a 27,000 DWT tanker for each of the three systems studied, and are graphically indicated in Figure 6. As illustrated, the initial installation/application costs for these systems vary considerably, and are $465,000,[5] $349,500 and $162,000, respectively, for the all-coating, coating/anode and all-anode systems. For a 10-year protection period, it is estimated that the all coating system will cost $553,000,[6] the coating/anode system $500,500 and the all-anode system $476,000. However, since these systems do not provide the same degree of protection, these ten year costs should not be compared directly. Because the coating system will provide approximately twice the protection available from the all-anode system (coating offers essentially 100 percent protection, while only 50 percent protection is offered by the all-anode system), the 10-year cost of the coating system should be compared with the 20-year cost of the all-anode system in order to be realistic. Such a comparison makes the all-coating system (and the coating/anode system to a lesser degree) exceedingly attractive from the total cost standpoint alone.

The operation of full-scale cathodic protection systems during the past three years together with our recent experience with coating systems on Esso Standard Oil Company vessels has emphasized the numerous advantages and disadvantages inherent in each system. Pertinent to the cost study presented, advantages and disadvantages are listed below:

Full-Scale Coating System

Advantages

1. Maximum protection (essentially 100 percent) against corrosion is obtained.
2. Offers control of corrosion under clean, dirty and specialty service conditions.
3. For successful operation, system requires little or no attention on the part of the crew and practically no follow-up from the shore staff.
4. Weight of coating system is less than that of other available protection systems.

[5] The chemical inhibitor spray system for protection of non-ballast tanks on the larger vessels is not considered practical, because of the physical configuration of the tank structure. A complex nozzle arrangement would have to be used to provide adequate "wetting" to all of the structure. In addition, a large volume of inhibitor solution would be required for spray application on these larger vessels.

[6] This cost figure does not include value of vessel's excess repair time required for large-scale coating application.
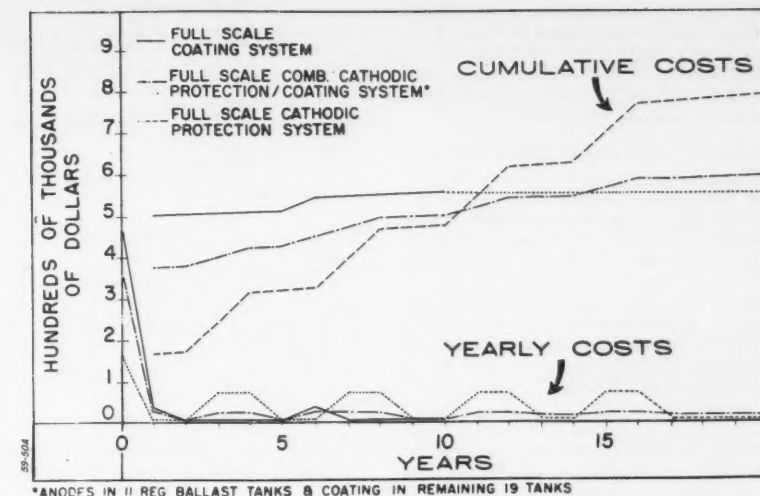
Figure 6—Estimated and cumulative costs, full-scale corrosion control system, 27,300 dwt clean service vessel.

5. Minimum maintenance is required after initial application.
6. The coating minimizes danger of contamination between grades and permits greater flexibility in consecutive scheduling of "touchy" grades of cargo. Coated tanks also facilitate transfer of vessels from dirty to clean service.
7. Coating system facilitates tank cleaning and gas freeing operations by eliminating scale removal and permitting shorter and lower temperature washing water to be used. See Figure 7.
8. Minimizes maintenance of cargo valves due to elimination of scale.

Disadvantages

1. High initial cost "ties-up" money that might be used for some other purpose.
2. The total effective life-span of the most successful coating materials is unknown. If life of system proves to be short, this method of corrosion control may be more expensive than other methods.
3. If application of coating is made during annual repair period, the number of tanks coated is limited to available repair time.
4. "Hot work" on coated structure necessitates subsequent coating repair.

Full-Scale Anode System

Advantages

1. Complete system usually can be installed during normal repair period of vessel (no extra time required).
2. System is easily maintained during annual repair periods of vessel.
3. For successful operation, system requires less attention on part of crew than do inhibitor spray systems.
4. System descales internal tank surfaces and maintains them scale-free during life of system.
5. Due to reduced scale, tank cleaning and gas freeing operations are facilitated.
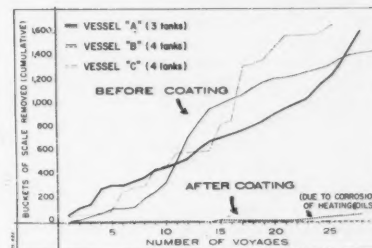
Figure 7—Removal of scale. Cargo tanks—before/after coating.

Disadvantages

1. Only limited protection (50-80 percent) is available—depending upon ballast system used.
2. For successful operation, system requires more attention on the part of the crew and shore-staff than does the coating system.
3. The weight of the full-scale anode system is more than that of either the all-coating system or combination coating/anode system.
4. Safety precautions must be observed to handle the hydrogen evolution problem.
5. Cannot be used in compartments which cannot carry salt water ballast (i.e. specialty tanks).
6. "Rotated ballast pattern" procedures frequently interfere with normal vessel routine.
7. Full-scale cathodic protection systems for the larger vessels may not be practical because of amount of ballast required to be carried each voyage.
8. Excessive calcareous deposits are sometimes obtained and require removal from the tank periodically.
9. Cathodically protected tanks do not offer same flexibility of scheduling cargoes as do coated tanks.

As shown, the use of protective coatings in cargo tanks has many advantages over other methods of corrosion control currently used. While their principal dis-

advantages may temporarily discourage their complete acceptance and full-scale use, it is expected that as more experience is obtained with tank coatings these disadvantages will be substantially minimized or eliminated entirely.

Coating Application Requirements

Successful application of any protective coating to internal cargo tank structure requires careful pre-planning and scheduling. Staging, lighting, ventilation, sandblasting and sand-removal equipment, rain shelters, etc. must all be arranged properly and used to permit the coating application to proceed without difficulty. To assist shipyard personnel in application of coatings on any vessel, detailed instructions should be prepared for shipyard guidance.

Discussion of these instructions with the shipyard before starting the coating application has been found most helpful and desirable. The assignment of a number of coating inspectors to each coating job has been found necessary to assure that proper application procedures are followed. The increasing demand for tank coatings together with the accumulative experience of shipyards with tank coatings should result in highly specialized and more efficient application procedures.

Conclusion

The existing full-scale anode and anode/inhibitor spray protection systems already in operation on Esso's 16,000 DWT tankers are believed to be providing sufficient protection against corrosion to substantially minimize or eliminate entirely reconditioning repairs and/or extend available clean-service life. However, the many advantages inherent in tank coating systems make the full-scale coating or coating/anode systems most desirable for the larger clean-service tankers. More extensive use of protective coatings in cargo compartments of not only Esso tankers but of vessels of other companies as well, appears likely during the coming years.

Bibliography

Symposium on Control of Internal Corrosion of Tankers. *Corrosion*, 9, No. 11, 388-422 (1953) Nov.

Recent Navy Experience with Saran and Vinyl Coatings. By W. W. Cranmer. *Corrosion*, 12, No. 5, 245-46t (1956) May.

Some Considerations in the Economics of Tanker Corrosion By C. P. Dillon, Carbide and Carbon Chemicals Co. Texas City, Texas. *Corrosion*, 12, No. 9, 67-69 (1956) Sept.

Cathodic Protection of Internals of Ships. By L. P. Sudrabin. *Corrosion*, 13, No. 7, 466t-472t (1957) July.

Countermeasures for Internal Corrosion of a Tanker Ship. By Charles P. Dillon. *Corrosion*, 11, No. 9, 393t-405t (1955) Sept.

Improved Methods Plus Hot Spray Speed Application of Saran Coatings. By Harland A. Morley. *Corrosion*, 15, No. 3, 116-117 (1959) March.

Corrosion Prevention in Tankers and Storage Tanks by Fogging or Flotation With an Inhibitor Solution. By J. C. D. Oosterhout, Maurice J. Stanley, Texaco, Inc., Port Arthur, Texas and W. S. Quimby, Texaco, Inc., Beacon, N.Y. *Corrosion*, 15, No. 5, 241t-244t (1959) May.

DISCUSSION

Question by A. L. Alexander, U. S. Naval Research Laboratory, Washington, D. C.:

The Navy has been using organic coatings for cargo holds of tankers for about 10 years. Do you have comparative costs and performance data between inorganic and organic coatings?

Reply by J. F. Koehler:

The majority of the tank coating applications on Esso Standard Oil Company's vessels has been made with inorganic coatings. Only few small-scale shipboard tests (1000 sq. ft./coatings) have been made with organic materials. In view of the short duration of these tests, however, sufficient data has not yet been obtained to permit any comparison between the performance of inorganic and organic type coatings.

Question by A. R. Cook:

In your judgment of these different protection systems, what were your criteria of success and also do you have any specific recommendations as to the best techniques available to judge relative corrosion rates in clean and crude oil cargo tanks?

Reply by J. F. Koehler:

Evaluation of the effectiveness of the experimental corrosion control systems used on Esso Standard Oil Company's clean oil tankers has been based primarily on comparison of corrosion rates (obtained from consecutive ultrasonic thickness measurements of the tank structure over a period of three years) in adjacent protected and non-protected tanks. However, visual observations, test panel corrosion-rate measurements, scale removal records, etc. were used also to supplement such primary information in the analysis of the protection systems under study. It is generally agreed that the best techniques available to evaluate protection systems in clean and crude oil cargo tanks include:

1. Comparison of corrosion rates obtained from consecutive ultrasonic thickness measurements of adjacent protected and non-protected tank structure. To assure maximum accuracy, special care should be taken in the preparation of measurement surfaces and in the operation of the measuring unit. In addition, the measurements should be taken over a period of several years to minimize errors common to the use of this type instrument.

2. Comparison of test panel corrosion rates measured in adjacent protected and non-protected tanks.

3. Pit measurements (crude service corrosion): The severity and frequency of pitting type corrosion should be measured. Pit depths, plaster casts and photographs should be used in evaluation of this type corrosion.

4. Potential measurements in cathodically protected tanks.

5. Visual observations of protected and non-protected tanks. The inspection should always be carried out by the same observer.

6. A review of operating data, such as types of cargoes carried, machine washing time and temperature, ballast time, etc. This information should be considered in relation to the above.

New Instruments and Techniques for

Ultrasonic Measurement of Tank Ship Corrosion Losses*

By DWIGHT J. EVANS

Abstract

A method of making nondestructive thickness measurements from one side on steel, especially in tank ships, using an ultrasonic gauge, is described. Accuracy of the "slide rule" method of calibration is detailed, and the various sources of error examined and means of compensating for them explained. Merits of the cathode ray tube resonance instrument are explained and its efficiencies over earlier instruments outlined.

New techniques developed during experience in recent years are described and some changes in attitude toward earlier accepted procedures explained. Manner in which data are recorded is shown in tables.   2.4.3

Introduction

PREVENTION or mitigation of the multi-million dollar corrosion losses in sea-going tankers has become a major activity among shipowners during the past ten years. Corrosion control measures include cathodic protection, coatings, inhibitors, spray systems and de-humidifiers. There is a conflict of opinion as to the merits of various systems—primarily the result of non-standardized evaluation methods and perhaps different operating conditions. Obviously, there is a need for an accurate standardized method of evaluation acceptable by all.

Visual examination, measurements of pit depths, profiling,[1] test panels, and nondestructive thickness measurement are all used for evaluation and all have merit. In the case of nondestructive thickness measurements, with which this article is primarily concerned, there is a wide diversity of results, due primarily to the instruments used and various levels of ability and training of instrument operators. In general, ultrasonic test instruments are most suitable, but standard operating procedure with ultrasonic instruments is not sufficiently accurate for a reasonably correct evaluation. One ultrasonic gauge's accuracy using standard operating procedure is about ± 5 percent, assuming that the instrument is properly tuned and calibrated and that the operator is able to obtain a reliable reading. Errors of this magnitude are excessive when it is necessary to determine corrosion rates of a few thousandths of an inch in a .500-inch plate.

Special techniques for improving ultrasonic gauge accuracy to within 1 percent have been developed and used by the writer's organization. Some of the techniques have been described in an earlier paper[2] and some new developments will be explained here. Also, experience with new direct reading ultrasonic equipment now used almost exclusively for major surveys, will be covered. Techniques with these instrumnts are suggested as a basis for a standardized test program.

Obviously, nondestructive thickness measurement of the steel plates cannot be used for evaluating protective coatings. However, a complete thickness survey often is made before coatings are applied to determine actual condition of the vessel. Coating evaluation is primarily visual and nondestructive film thickness gages are used as an aid.

Method of Obtaining Measurements

The principles of operation of ultrasonic measuring equipment are illustrated in Figures 1, 2 and 3. Figure 4 shows the principles of the "slide rule" method of taking measurements. While this illustrates a standard rule using the C and D scales, special slide rules having harmonic numbers, velocity constants and thickness designations will be available soon.

Both accuracy and reproducibility are within one percent, provided that the instrument is used by a trained operator, the slide rule method is employed, low carbon rolled steel plates such as are commonly used for ship construction are measured, thicknesses measured are on the order of .125 to 1.000-inch, test frequency range is constant and that instruments are accurately calibrated on identical test blocks. This is substantiated by actual data. If the listed variables are controlled, then greatest source of error is slight variations in apparent and/or actual sound velocity through the material measured. The apparent change seems to vary with thickness measured (that is, harmonic number if same frequency range is used), and apparently changes from about 232,000 inches/second for low harmonic numbers to about 235,000 inches/second (approximately 1 percent) for the higher harmonic numbers (above the tenth harmonic, in the range of .750-inch and above). This change is probably due to wave cancellation or reinforcement. In any event, a correction can be made on the slide rule for the various thickness ranges.

Variations in actual velocity constant are a possible source of error, and is the subject of controversy among various users of the equipment. Except for a few rare instances, this variation has been found by the writer to be well within one percent on steel plates used for tankers. Sound velocity is a function of modulus of elasticity and density, and Poisson's Ratio[3] as shown in Figure 5. So far, the greatest variation observed in tests on hundreds of tank ships was in the steel plates of a 45-year-old vessel. In this case, the sound velocity constant was 234000 inches/second rather than 232000 inches/second an error of .8 percent. In this case, as in all cases where a velocity variation is indicated or suspected, the velocity constant to be used is accurately determined by measuring thickness with a micrometer and following the slide rule procedure in reverse to establish the velocity constant.

Figure 5 also illustrates the effect of scale on the opposite surface. Any difference in acoustic impedance (product

DWIGHT J. EVANS established Engineering Test Services, Inc., Tulsa, Okla., which specializes in ultrasonic thickness measurement for corrosion analysis. He formerly was associated with the Engineering Test Division of Phillips Petroleum Company and with Branson Instruments, Inc. He received a BS in electrical engineering at University of Kansas. He is a member of NACE.

About the Author

of velocity and density) results in a reflection and refraction at the interface and therefore a weak returned signal, but an accurate measure of steel thickness only. Under these conditions, the refracted wave is of no consequence, since it is directed away from the return path and in any event is again refracted at the interface.

If the scale is tight and acoustic impedances are nearly equal, however, the interface will be penetrated by the lower frequency waves. Frequencies below about one Mc tend to penetrate tight scale, depending upon its bond and composition and thus introduce an error in the overall average. This shift is apparent when the pattern of resonant frequencies and harmonic numbers are set up on the
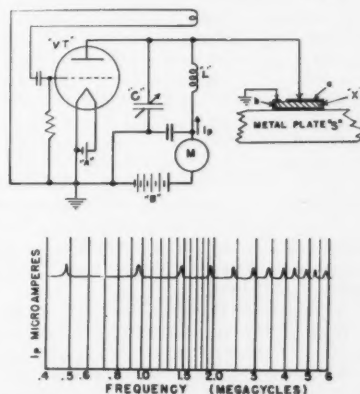
Figure 1—Top, Basic circuit for thickness gauge operating on ultrasonic resonance principle. Bottom, plate current as a function of frequency for ¼ inch steel thickness.

21
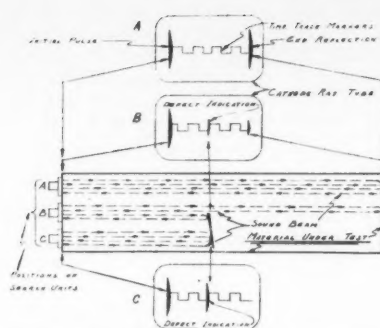
Figure 2—Longitudinal sound waves in a long shaft.

TABLE 1—Thickness Calculations Comparing the Accuracy of the Conventional Method and the Slide Rule Method.

Tube No.	Thickness Before Acidizing		Thickness After Acidizing	
	Conventional Method	Slide Rule	Conventional Method	Slide Rule
21	.441"	.428"	.422"	.422"
22	.343"	.340"	.334"	.333"
23	.414"	.389"	.396"	.384"
24	.418"	.398"	.419"	.387"
25	.418"	.414"	.400"	.405"
26	.393"	.391"	.396"	.390"
27	.397"	.384"	.386"	.380"
28	.453"	.445"	.443"	.437"
29	.428"	.413"	.414"	.412"
30	.43"	.408"	.404"	.399"
31	.441"	.387"	.396"	.386"
32	.446"	.412"	.407"	.408"
33	.40"	.380"	.389"	.378"
34	.374"	.354"	.349"	.354"
35	—	—	.394"	.397"
36	.40"	.414"	.411"	.408"

slide rule, but will not be detected if standard operating procedure is used. In practice, frequencies below 1 Mc are not used unless special considerations warrant it. In any case, if the pattern is checked on the slide rule an accurate thickness will result.

This phenomenon is usually not encountered in tank ships, but does occur frequently on "platformer tubes." In one particularly interesting case of a large number of readings obtained by others, using the standard technique, thickness readings obtained were erratic and were condemned. Fortunately, resonance frequencies had been recorded and on accurate set of readings were obtained by using the slide rule technique. A comparison of results obtained is shown in Table 1.

New Instruments and Accessories

A resonance type instrument using a cathode ray tube to visually indicate thickness has been successfully used since late 1957. The resonance indications are presented visually on a cathode ray tube in this device. Basic circuit is shown in Figure 6. A frequency scale calibrated directly in thickness and having a scale for each harmonic, is placed over the tube face. The resonances will appear at the same thickness on each scale, thus providing exactly the same checks as in the case of the slide rule method of calculating thickness.

Measurement characteristics are similar to those of the earlier instruments. When surfaces are badly corroded, or have tight scale on the opposite side, high gain settings are required and spurious signals appear on the screen. In such cases, interpretation is comparable to interpretation of resonances with the slide rule. The

$$\text{THICKNESS (STEEL)} = \frac{116}{f_n - f_{(n-1)}}$$

f_n = FREQUENCY AT THE nth HARMONIC.

$f_{(n-1)}$ = FREQUENCY AT THE $(n-1)$ HARMONIC.
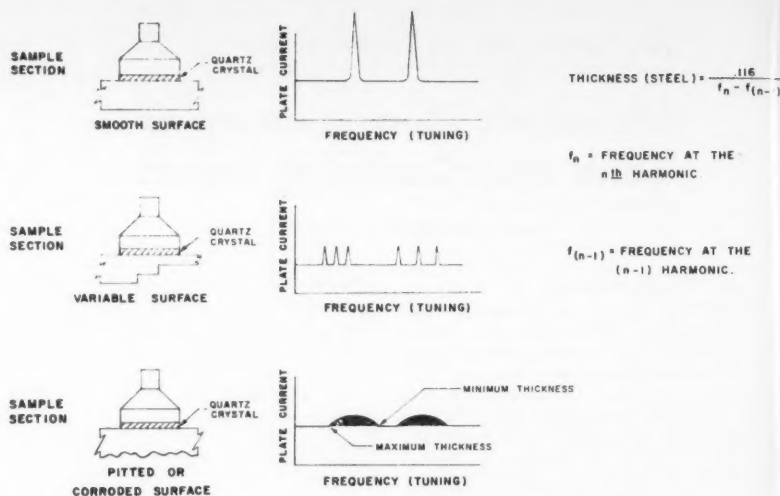
Figure 3—Resonance frequencies obtained with various surface conditions.

1. From basic theory, it is known that the frequency of each Resonance (Harmonic) obtained in an Audigage test must be an exact multiple of a common fundamental frequency. Further, the difference between any two adjacent harmonics should be equal to this fundamental frequency.

2. Therefore, each harmonic should be an exact multiple of the difference between any two obtained with the Audigage.

3. A simple slide rule method of verifying this relationship, determining an accurate fundamental frequency, and obtaining an accurate thickness has been devised as follows:

   EXAMPLE 1. Harmonic Frequencies obtained: 1.80 Mc., 1.50 Mc., and 1.20 Mc.
   Difference Freq. (Fundamental): .30 Mc.

   Check on Slide Rule, and obtain thickness as follows:

A. Set index end of "C" Scale on .30 (Avg. Diff.) on "D" Scale.

B. Observe that 1.80 is 6th Harmonic, 1.50 is 5th, and 1.20 is 4th, with perfect alignment. Therefore, resonances are accurate and .30 is an exact difference.

C. To obtain thickness, (steel) move slide indicator to .116 on "D" Scale, and read thickness of .387" on "C" Scale.

4. In most cases, multiples such as those above will not be encountered. For example, if harmonic values are 1.84 Mc., 1.54 Mc., and 1.24 Mc., a difference of .30 Mc. is still obtained, but these values are obviously not exact multiples of .30.

5. A more nearly correct difference will be obtained by moving the "C" Scale so that the 6th harmonic coincides with 1.84 Mc., the 5th with 1.535 Mc., and the 4th with 1.23 Mc. A thickness of .378" is then obtained, as compared to a thickness of .387" if it had not been corrected. In practice, the harmonic number is aligned with the strongest signal.

6. If readings such as 1.95, 1.65, and 1.35 are obtained, it is obvious that they are not harmonics of the difference (.30 Mc. as in previous examples), and the reading is discarded.

Figure 4—Precision measurements by use of a slide rule.

$$R_E = \left[\frac{P_1 V_1 - P_2 V_2}{P_1 V_1 + P_2 V_2} \right]^2$$

P_1 = DENSITY OF STEEL.

V_1 = SOUND VELOCITY IN STEEL.

P_2 = DENSITY OF COKE.

V_2 = SOUND VELOCITY IN COKE.

R_E = RATIO OF REFLECTED TO INCIDENT ENERGY.

$$V_L = \sqrt{\frac{E}{P} \cdot \frac{(1 - \sigma)}{(1 + \sigma)(1 - 2\sigma)}}$$

V_L = LONGITUDINAL WAVE VELOCITY IN CM/SEC.

E = YOUNG'S MODULUS OF ELASTICITY.

P = DENSITY IN GM/CC.

σ = POISSON'S RATIO.
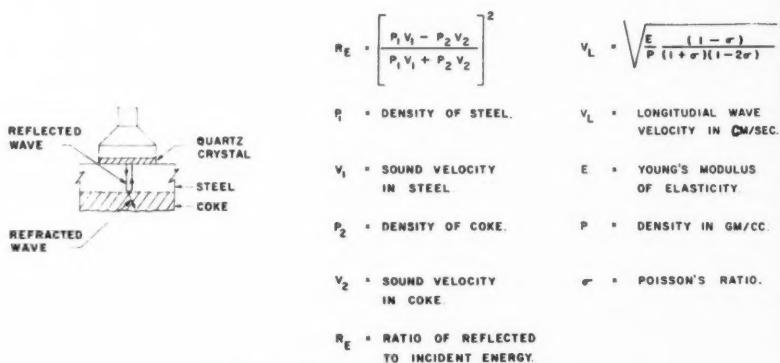
Figure 5—Effect of backup materials on ultrasonic waves.

instrument is comparatively bulky, an extension cable between the instrument and transducer and connecting telephones, makes it practical. Figure 7 illustrates the instrument set up on the

deck of a tanker. The cathode tube instrument has numerous advantages, particularly when more than a few hundred readings are required. Thickness readings are direct and the operator has time

Figure 6—Schematic circuit for cathode ray tube ultrasonic resonance device.

Figure 7—Showing cathode ray tube device on location and operator recording data.

	Ultrasonic Resonance	Ultrasonic Resonance	Ultrasonic Pulse
TYPE			
METHOD OF OPERATION	Manual tuning	14" or 21" cathode-ray tube presentation.	5" cathode-ray tube presentation.
ACCURACY	Within 1% on corroded surfaces when "slide rule technique" is used.	Within 1% on corroded surfaces. 1/10 of 1% on smooth surfaces.	Approximately 3%–5% under field conditions.
OPERATING WEIGHT	Eighteen pounds.	Sixty pounds.	One-hundred pounds.
POWER REQUIREMENTS	Self-contained batteries.	110 volt, 60 cycle, a/c.	110 volt, 60 cycle, a/c.
ADVANTAGES	Used when readings are at scattered locations. Portable and can be carried by operator. Average thickness comparable to "loss of weight" method of determining corrosion rate is obtained when opposite surface is uniformly corroded (Pits up to .125" in depth).	Used when large number of readings required in relatively small area. Up to 1000' of extension cable between transducer and instrument can be used. Direct, instantenous readings provide high testing rate. Characteristics on corroded materials comparable to Audigage "slide rule technique." Central test location is less fatiguing to operator, and assures time for recording notes, etc.	Best adapted for thickness measurement of heavy materials such as submarine plates, and for flaw detection in welds, shafts, etc.
DISADVANTAGES	Operator must be highly trained, and of at least technician caliber. All readings must be calculated by "slide rule technique" for 1% accuracy.	Comparatively heavy and cumbersome and requires more "set-up" time. Two trained operators desirable for corrosion measurements. Direct reading scales have limited thickness range.	Not practical for thickness measurements of about 3/8" and under. Heavy and cumbersome. Extension cables over about 25' in length cannot be used. Instrument not designed for thickness measurements, special scales must be constructed.

Figure 8—Principal characteristics of three major ultrasonic test instruments.
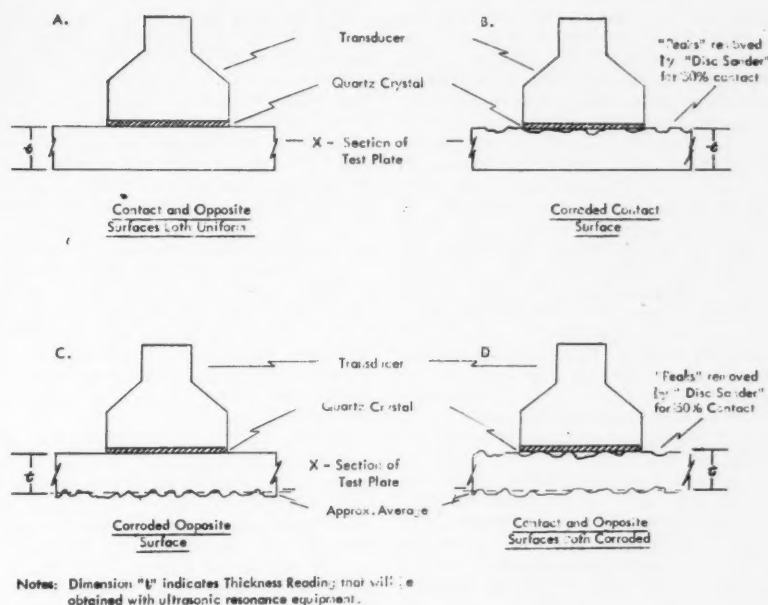
Notes: Dimension "t" indicates Thickness Reading that will be obtained with ultrasonic resonance equipment.

Figure 9—Characteristics of ultrasonic thickness measurements.

to record data, make special notes and compare with previous data. One of the intangible and important benefits is the psychological effect on inspectors, owners or others who may be witnessing the tests. Thickness readings are clearly seen by all and there can be no question as to authenticity.

The testing rate is much more rapid than with the earlier instrument when readings are within the radius of the extension cord. For tanker operations, a 125-foot extension cable is used and usually, it is possible to measure all bulkhead plates, shell plates and frames in six tanks with one instrument location.

The relative merits of the various types of instruments are shown in tabular form in Figure 8.

Improvements in transducers for both types of instruments have been an aid in obtaining difficult readings. This includes the "Type Z" transducer, which has the sensitivity several times better than standard quartz transducers.

New Techniques Aid Precision
Importance of Test Locations

Compared to thickness measurement of piping, chemical plants, etc., measurement of tanker plates is difficult. It is interesting to note that in earlier literature, it was assumed that accurate relocation was not necessary because an average corrosion rate only was measured.[2] It soon became evident, however, that accurate relocation of test spots was vital, so beginning in 1954, all test locations were accurately marked by various methods, such as weld beads, measurement, or by permanent markers such as saturated polyester film.

TABLE 2—Showing the manner in which data are recorded.

Note: Audigage Resonances designated as follows:

P = Poor Signal
M = Medium Signal
G = Good Signal

Plate Thickness of Typical Transverse Cargo Tank Bulkheads – Port, Center, and Starboard Tanks

S.S. _____

Original Thickness for Sun Built T-2 Tanker

After ___ Trans. BHD. No. 2 Tank

Transverse Bulkhead Plate	Thickness of Construction	PORT Audigage Resonances		Thickness	% Wastage	CENTER Audigage Resonances		Thickness	% Wastage	STBD. Audigage Resonances		Thickness	% Wastage
Top Plate	.461"	1.82 1.47	P	.319"	30.8	1.83 1.22 1.52	M	.380"	17.6	1.90 1.11 1.53	P	.306"	33.6
1st Strake	.461"	1.73 1.38	P	.337"	27.0	1.95 1.31 1.63	M	.356"	22.7	1.80 1.07 1.14	P	.322"	30.2
2nd Strake	.380"	1.79 0.90 1.33	M	.261"	31.3	1.99 1.20 1.60	G	.290"	23.6	1.80 0.91 1.35	G	.252"	32.2
3rd Strake	.420"	1.86 1.12 1.48	M	.314"	25.3	1.71 1.03 1.34	G	.339"	19.3	1.64 1.10 1.46	G	.319"	24.0
4th Strake	.440"	2.00 1.34 1.67	G	.347"	21.2	1.85 1.22 1.53	G	.381"	13.4	1.93 1.30 1.61	G	.360"	18.2
5th Strake	.461"	1.85 1.74 1.54	G	.375"	18.6	1.76 1.15 1.47	G	.395"	14.2	1.83 1.28 1.52	M	.382"	17.2
6th Strake	.500"	1.95 1.41 1.68	G	.414"	17.1	1.85 1.33 1.59 1.96	G	.440"	12.1	1.91 1.37 1.63	P	.410"	18.0
7th Strake	.520"	1.80 1.31 1.55	M	.451"	13.3	1.93 1.46 1.70 1.22	G	.477"	8.2	1.77 1.36 1.52	M	.458"	12.0
Bot. Plate	.540"	2.00 1.50 1.75 1.25	G	.464"	14.0	1.92 1.45 1.69 1.21	G	.481"	11.0	1.78 1.27 1.53	G	.456"	15.5

Figure 10—Typical corrosion rates determined by ultrasonic measurements. Note projected curve indicated probable life of plate.

Random locations cannot be used because corrosion rates vary at different elevations in a tank. The rate may be much higher at the top than at the bottom of any given plate, particularly in the top plate, because of different exposures to ballast water, fuel or fuel vapors, etc. Also thickness of rolled steel plates usually is greater in the center than at the edges. This condition, known as "camber" is a characteristic of the original plates and is encountered almost always when precision thickness measurements are made. When the plates are rolled, slight deflection in the rolls and other variables produce this difference in thickness. It may be assumed that minimum specified thickness is maintained near the edge of the plate. Maximum permissible tolerances are specified by American Society for Testing Materials as a variation from specified plate thickness. For example, permissible minimum thickness of a plate .375-inch thick and 6-feet wide (when ordered to thickness) is .365-inch, or .010-inch under and permissible excess in average weight is 7 percent over. If ordered to weight (15.3 lb.), permissible variations are 3.0 percent under and 4.5 percent over average weight.

In view of these variations establishment of definite test locations is imperative. Standard patterns for test locations have been established for T-2 tankers, T-3 tankers and various vessels of the super tanker class. It is standard policy now to mark exactly all test locations even on routine surveys, even though the owner may advise that only one set of readings ever will be required. Later decisions often are made to repeat the readings, or to embark on a corrosion control analysis program. If previous locations are unknown, results are useless for an accurate analysis.

Surface Preparation is Critical

Surface preparation at the test location also is a critical factor and must be uniform each year. The metal removed in cleaning must be controlled within the accuracy of the test equipment, that is, within .001 to .002-inch if results are to be useful. Proper surface preparation is

shown in Figure 9. An ultrasonic test requires a reasonably flat surface of about 2 or 3 inches in diameter in order to obtain good transmission of the sound waves into the material. Scale or other corrosion products must be removed with a chipping hammer and the peaks of a normally corroded surface removed so that about a 50 percent contact area is provided. A "disk sander" should be used for this preparation, rather than a grind wheel. The surface obtained with a grind wheel is never quite flat. Further, a grind wheel usually removes metal excessively. Obviously apparent corrosion rate increases drastically when a grind wheel is in the hands of an over-ambitious worker, particularly in "easy to reach" locations. When accurate corrosion measurements are to be made, supervision of surface preparation by test personnel is essential.

It often is desirable to know the corrosion rate on both sides of a bulkhead, particularly on those separating protected and unprotected tanks. A method of completely protecting the measurement area on one side is necessary for evaluation of rate on the opposite side, because otherwise the total metal loss is measured. Of the various methods developed, one is the use of a saturated polyester film patch approximately 0.001-inch thick and 6-inches in diameter. The film has an adhesive on the back and is imprinted on the face with the exact test locations and size of the transducer.

Judging from tests so far the plastic film method appears to be practical for protecting the measurement area on one side of the bulkhead. The first installations of this kind were made in 1954 and they have been continuous since then. About 90 percent of the film patches remain in place for a year, but approximately 15 percent of this number suffer damage and are replaced as a precautionary measure. Highest casualty rate is in cathodically protected tanks. Apparently the adhesive is attacked by the calcareous deposit. Even though the film is destroyed, the surface is protected from corrosion and satisfactory thickness readings are obtained. Resonance readings are taken through the film in the remaining

75 percent on subsequent years, thus greatly reducing survey cost, because the cost of cleaning the test location (usually at least 50 percent of the survey cost) is eliminated. When readings are taken through the film, a correction factor for its thickness is used so it is not a source of error.

Neoprene rubber pads, held in place by a block of wood securely attached to the plate with "hold down" studs is a completely satisfactory method. The studs are welded about 6 inches apart on either side of the test location, a neoprene pad is placed over the clean metal surface, then covered by a piece of wood, which is clamped in place. These pads provide effective protection but are expensive to install. Readings cannot be taken through the wood and neoprene, so the pads must be removed and replaced each time a test is made.

Access to Location is Problem

Access to test location is always a problem and the search for better methods continues. Standard shipyard staging is expensive, particularly when access to only one or two locations at the top of the tank is required, so every effort is made to locate test stations at points that can be reached with a minimum of staging. For example, in a T-2 tanker, very little or no staging is required for installations near the top of the bulkheads of port and starboard tanks if they are properly placed. Presently, the most widely used system is that of "baskets and hoists." This method was described in an earlier article.[2] Chief disadvantage, is the fact that a hole must be drilled in the deck at each tank. However, in some cases, the hole provides a convenient means of checking instrument calibration. Another access method involves baskets and hoists attached underdeck; with hoists usually operated by compressed air. In a few cases, rope blocks are attached underdeck. Planning and coordination by test personnel, owner and shipyard is always advisable before testing is started and will result in more satisfactory results at lower cost. Unless

TABLE 3—Type of Data Record Permitting Comparison of Successive Readings to Determine Rate of Wastage Over Period of Years.

PORT SIDE

Structural Member	Original	1953 Reading	1954 Reading	1955 Reading	1957 Reading	1958 Reading	Present Diff.	Present % Wastage
BHD. PLT. NO.								
1 (Top)	.50"	.456'	.443"	.434"	.419"	.401"		19.8%
2	.50		.441	.428	.402	.384		23.2
3	.42			.362	.347	.333		20.7
4	.42			.333	.322	.293		30.3
5	.44	.393	.390	.358	.335	.333		24.3
6	.48			.398	.381	.368		23.4
7	.54			.464	.436	.434		19.6
8	.58			.530	.521	.509		12.2
9 (Bot.)	.62	.627	.614	.600	.583	.578		06.8

STBD. SIDE

Structural Member	Original	1953 Reading	1954 Reading	1955 Reading	1957 Reading	1958 Reading	Present Diff.	Present % Wastage
BHD. PLT. NO.								
1 (Top)	.50"	.446"	.435"	.424"	.404"	.399"		20.2%
2	.50		.429	.410	.406	.382	.366	26.7
3	.42			.346	.338	.330		21.4
4	.42			.331	.302	.294		30.0
5	.44	.380	.372	.352	.332	.326		25.9
6	.48			.348	.324	.323		32.7
7	.54			.480	.456	.455		15.6
8	.58			.535	.512	.506		12.7
9 (Bot.)	.62	.631	.616	.602	.591	.584		04.2

thus
se the
usually
st) is
taken
or for
our e

pla e
ed to
is a
The
rt on
nec-
met: l
woo ,
pacs
e ex-
ot be
oren ,
d re-

prob-
thods
ng is
s to
op of
ort is
oints
m of
nker,
d for
bulk-
ks if
, the
'bas-
de-
Chief
must
low-
es a
ment
in-
der-
d by
rope
ning
wner
efore
more
nless

tting
s to
riod

esent % Wastage
19.8%
23.2
20.7
30.3
24.3
23.4
19.6
2.2
06.8

esent % astage
0.2%
6.7
1.4
0.0
5.9
2.7
5.6
2.7
4.2

expense is immaterial, measurement locations should be selected on the basis of obtaining representative corrosion rates at the most easily accessible locations.

Portable ladders are not recommended although they are occasionally used in cases when absolutely necessary. If so, they must be securely tied in place.

How Data Are Recorded

Table 2 shows how data are recorded. If previous surveys are to be compared, all thickness data are tabulated on a report form similar to the one shown in Table 3. If desired, an estimate of the anticipated life of a plate can be obtained by projecting a curve to its intercept with maximum allowable corrosion loss, shown in Figure 10.

Summary

Reasonably accurate corrosion rates in tank ships can be obtained by nonde-structive thickness measurement with presently available equipment, provided personnel using the equipment are highly trained, use the techniques described herein and are thoroughly familiar with the characteristics of their equipment. This includes the ability to adjust the instruments for maximum sensitivity and accurate calibration on special, uniform test blocks.

New types of instruments offer many advantages over older equipment and are now used for most major surveys.

A slight change in the sound velocity constant is a possible source of error, but experience indicates it does not exceed 1 percent. Corrections and/or compensation for this error can be made when the condition is known to exist. Further investigations should be made if this error is to be reduced and all data correlated by a central agency. These data should include actual resonance frequency readings obtained, so that it can be carefully analyzed by the slide rule technique.

Acknowledgment

References

1. J. R. Caldwell. Reduction of Tanker Ballast Space Corrosion Rates by Deoxygenation of the Ballast Water with Sodium Sulphite. *Marine Engineering/Log,* October 1958.
2. Dwight J. Evans. Corrosion Evaluation of Ship Bulkhead and Hull Plating by Audigage Thickness measurements. *Corrosion,* 11, No. 3 109t 114t (1955) March.
3. C. H. Hastings and S. W. Carter. Inspection, Processing and Manufacturing Control of Metals by Ultrasonic Methods. ASTM Special Technical Publication No. 101.
4. ASTM Designation A131-55. Standard Specification for Structural Steel for Ships.

Effects of Foreign Metals on

Corrosion of Titanium
In Boiling 2M Hydrochloric Acid*

By ROGER BUCK, III, BILLY W. SLOOPE and HENRY LEIDHEISER, JR.

Introduction

BECAUSE titanium has come only recently on the industrial metals scene, a limited amount of information and experience are available on its resistance to corrosion over a wide range of experimental conditions. This is particularly true in terms of knowledge of the effect of small amounts of metal ions in the corroding media and the effect of galvanic coupling to other metals under essentially anaerobic conditions. In two recent studies[1,2] in boiling HCl it was observed that foreign metal ions in solution and galvanic coupling yield very different results with titanium than with many other metals. For example, contact with the platinum metals decreases the corrosion of titanium to very low values, whereas with metals such as iron, nickel, tin and aluminum, to mention only four, contact with the platinum metals increases greatly the rate of corrosion. Along parallel lines Tomashov[3] recently has shown that additions of 0.1 to 1.0 percent of platinum and palladium to 18-8 stainless steels increase the corrosion resistance of this steel to attack by 20-50 percent sulfuric acid at 20 C.

The purpose of this study* was to expand information available on the effect of foreign metals on the corrosion of titanium and to make potential measurements in an attempt to explain these effects.

Description of Metals Used

The corrosion experiments were carried out in a 250-ml Erlenmeyer flask with a 19-inch long reflux condenser. The types of specimens used and the modifications in the experimental arrangement required for potential measurements will be described at the appropriate places in this report.

Aluminum was obtained as ½-inch rods. Purity was 99.9 percent.

Antimony was obtained as high purity chips and was cast into rods.

Bismuth was obtained as long castings in a purified grade.

Cadmium was obtained as ⅜-inch rods. Purity was 99.9 percent.

Cobalt was obtained as a small piece of a large ingot. Purity was 99.5 percent.

Copper was obtained as ⅜-inch rods. Purity was 99.999 per cent.

Gold was obtained as 1¼-inch cylinder. Purity was 99.9 percent.

Indium was obtained as ½-inch rod. Purity was 99.999 percent.

Iridium was obtained as a ¼-inch cylinder. Purity unknown.

Iron was obtained as ½-inch rods. Purity was 99.92 percent.

Lead was obtained as pigs. Purity was 99.998 percent.

Nickel was obtained as ⅝-inch rods. The rods contained 0.005 percent C, less than 0.009 percent Si, less than 0.01 percent Fe, less than 0.001 percent Mg, 0.17 percent Co, a trace of Cu and no Ti or Mn.

Nickel-copper alloys were made from the elements under an argon atmosphere.

Palladium was obtained as a ¼-inch rod. Purity unknown.

Platinum was obtained as a ¼-inch rod. Purity unknown.

Silver was obtained as a ⅝-inch rod. Purity was 99.99 percent.

Tin was obtained as 1-pound sticks. Purity was 99.998 percent.

Titanium was obtained in the form of ⅝-inch rods from several sources as described later. The majority of the experimental work was carried out on A70 commercially pure material. It contained 0.03 percent N and less than 0.10 percent C.

Vanadium was obtained as irregular pieces. Purity unknown.

Zinc was obtained as ⅜-inch rods. Purity was 99.999 percent.

Zirconium was obtained from Dr. M. L. Picklesimer of the Metallurgy Division, Oak Ridge National Laboratory. The raw material was crystal bar zirconium which had been arc-melted and rolled to ½-inch diameter.

Results

Corrosion of Titanium from Several Sources

In a series of preliminary experiments, specimens from four different sources were corroded in boiling 2M HCl for two hours and weight losses were determined. These specimens were as follows:

Sample 1. This sample was obtained from Dr. M. L. Picklesimer of the Metallurgy Division, Oak Ridge National Laboratory. The raw material was crystal bar titanium manufactured several years ago. The crystal bar was arc-melted in an argon atmosphere and then rolled to ⅜-inch diameter.

Sample 2. This material was crystal bar titanium. The as-purchased material was arc-melted in an argon atmosphere, swaged, and finally centerless ground to approximately ⅜-inch diameter.

Sample 3. This material was purchased in 1953 as commercially pure

W. ROGER BUCK, III, is a senior research chemist at the Virginia Institute for Scientific Research, Richmond, Virginia. He received a BS in chemistry from the University of Richmond in 1935 and a master's degree in physical chemistry from Duke University in 1940. Before coming to the Institute in 1952 he did college teaching. He is a member of the American Chemical Society, The Electrochemical Society and The National Association of Corrosion Engineers.

Buck

Sloope   **Leidheiser**

BILLY W. SLOOPE is Associate Professor of Physics at the University of Richmond and part time research scientist at the Virginia Institute for Scientific Research. He holds the PhD in Physics from the University of Virginia. His research interests include metal surfaces and the properties of thin films of metals.

HENRY LEIDHEISER, JR., is Director of Research of the Virginia Institute for Scientifc Research, a laboratory devoted to fundamental research in the physical sciences. Dr. Leidheiser holds the PhD in physical chemistry from the University of Virginia. His research interests are broadly in the field of the surface properties of metals and specifically in the fields of electroplating and corrosion.

Abstract

The rate of corrosion of titanium was determined in boiling 2M HCl when contacted to aluminum, cadmium, tin, zirconium, lead, bismuth, mercury, silver, copper, antimony, vanadium, 70:30, 50:50 and 30:70 copper-nickel alloys, iron, palladium, cobalt, nickel, gold, rhodium, platinum and iridium. Less extensive corrosion measurements of the same type were also made in 0.6 and 2M H_2SO_4. The potentials of the couple and of the two members of the couple were determined in boiling 2M HCl for 20 of the systems studied. A plot of the corrosion rate vs the couple potential yielded a polarization curve which was similar to the anodic polarization curve for titanium with an impressed voltage. The curve exhibited a maximum in corrosion rate at a couple potential of —0.49-volt vs the saturated calomel electrode. The potential of titanium in boiling 2 M HCl was also determined as a function of concentration of the following metallic cations in the acid: copper, silver, antimony, nickel, gold, palladium, rhodium, platinum and iridium. The influence of the cations on the corrosion rate was explained in relation to the polarization curve.   6.3.15

titanium. It was very hard and machined poorly, indicating a high level of contamination.

Sample 4. This material was purchased in 1957 as commercially pure A70 titanium. It was not unduly hard and machined readily. An additional supply was purchased in 1958 and this latter material had a slightly higher corrosion rate than the 1957 material.

Figure 1—The corrosion of titanium in boiling 2M hydrochloric acid when coupled externally to a second metal.

Figure 2—The relative potentials of titanium, the second metal and the couple in boiling 2M hydrochloric acid.

Figure 3—Time-potential curves for thirteen titanium-second metal couples in boiling 2M hydrochloric acid.

Results obtained in this study are given in Table 1. This tabulation indicates that in any one kind of titanium a high fraction of the results occur within a narrow range of corrosion rates, but a significant fraction (20-30 percent) of the results are inconsistent with the majority. The average corrosion rates of the Samples 1, 2 and 4 titaniums did not differ a great deal but the values of the Sample 3 were significantly higher. This higher rate is presumably associated with the lower purity of this titanium. In the experiments reported in references 1 and 4, the Sample 3 material was used, but in the majority of the experiments reported herein and those reported in Reference 2, the Sample 4 material was used.

Corrosion of Titanium in Boiling Acids When Coupled to Another Metal

Preliminary experiments were carried out on titanium samples which were machined in the shape of a cylinder with a threaded hole in one end. The second metal was machined as a cylinder with a threaded shaft. When assembled, the resulting cylinder had a surface area of approximately 3.2 cm² with equal areas of the titanium and second metal exposed. Before an experiment, the separate cylinders were etched in acid so that a similar surface to that formed during the corrosion experiment would be present at the start. Results of these experiments in 2M HCl, 2M H₂SO₄, and 0.6M H₂SO₄ are summarized in Table 2. It will be noted particularly that the results in 2M HCl and 0.6M H₂SO₄ were comparable except for gold, palladium and nickel. These three metals were inactivators in HCl and were activators in 0.6M H₂SO₄. In 2M H₂SO₄ all the metals were activators except iridium, which was a very effective inactivator and reduced the corrosion rate to a negligible value.

It was next of interest to relate the potential of the couple to the corrosion rate. For this purpose an assembly was used in which the potential of the bi-metallic couple at the boiling point could be determined vs a saturated calomel electrode. The calomel electrode was immersed in a small vessel which was filled with the corroding solution and was maintained at room temperature. The small vessel was connected to the corrosion cell by a short length of capillary tubing. In these experiments, run for two hours in some cases and for four hours in others, the corrosion rates of the ti-

tanium specimen and the second metal were determined by weight loss at the end of the experiment. Results of these studies are shown in Figure 1. The corrosion rates in these 21 instances fell along a smooth curve with a maximum in corrosion rate at a potential of approximately —0.49 vs the saturated calomel electrode.

The results shown in Figure 1 and those listed in Table 2 are not identical, presumably because of the difference in experimental arrangement. However, there are no serious differences between the two kinds of measurements.

In another series of experiments the potentials of the second metal, the titanium and the couple were determined. It was impossible in these experiments to determine a meaningful corrosion rate because the times that the samples were coupled externally varied depending upon the second metal being studied. The results of these experiments are shown in Figure 2. In Region A, represented by the cadmium and aluminum couples, the second metal was anodic to titanium and the potential of the couple was intermediate to the uncoupled potentials of the two metals. In Region B, represented by tin, zirconium, lead, bismuth and mercury, the potential of the couple was identical to that of titanium. In Region C, represented by silver, copper, vanadium and antimony, the potential of the couple was intermediate to that of either metal alone and was cathodic to titanium alone. In Region D, represented by the copper-nickel alloys, iron, nickel, cobalt, gold, palladium, iridium, rhodium and platinum, the potential of the couple was identical to that of the second metal.

In Figure 3 typical potential-time curves are shown for a number of the titanium-metal couples. Gold, silver and palladium were unusual in that the potential of the couple changed appreciably with time. Additional studies of this phenomenon are now in progress because of the recent discovery that in gold-tin, silver-tin, gold-cadmium, gold-lead and palladium-lead couples, the noble metal becomes covered with a deposit of unknown composition.

TABLE 2

The Relative Effectiveness of the Various Metals in Boiling HCl and H₂SO₄ in Altering the Corrosion Rate When Coupled to Titanium. (Values in Parenthesis Are Rates Relative to Those of Uncoupled Blank.)

2M HCl	2M H₂SO₄	0.6M H₂SO₄
Antimony (2.86)	Nickel (2.53)	Silver (3-13)
Vanadium (2.64)	Palladium (2.37)	Vanadium (3.00)
Copper (2.57)	Gold (2.34)	Gold (2.78)
Silver (2.57)	Copper (2.34)	Copper (2.71)
	Iron (2.18)	Antimony (2.29)
Lead (1.75)	Silver (2.07)	Iron (2.12)
Tin (1.54)		
Iron 1.50)	Rhodium (1.66)	Nickel (1.83)
Indium (1.29)	Platinum (1.45)	Cobalt (1.83)
	Indium (1.44)	Lead (1.54)
Cobalt (1.10)		Palladium (1.50)
Bismuth (1.07)	Lead (1.09)	Tin (1.33)
Cadmium (1.04)	Bismuth (1.06)	
Aluminum (0.96)	Tin (1.05)	Bismuth (1.25)
Nickel (0.86)		Cadmium (1.12)
	Iridium (0)	Zinc (1.08)
Gold (0.14)		Mercury (1.00)
Palladium (0)		
Rhodium (0)		Rhodium (0)
Platinum (0)		Platinum (0)
Iridium (0)		Iridium (0)

TABLE 1—Average Corrosion Rate in Mg./Cm.²/Hr. for Titanium Specimens Corroded in 2M HCl at the Boiling Point for 2 Hours

	SAMPLE							
	1	**2**		**3**		**4**	
	1.8	1.2	1.9	5.0	2.7	1.4	1.9
	1.9	1.9	1.2	3.0	3.3	2.8	3.6
	2.3	1.2	1.1	2.4	2.2	1.4	2.4
	1.0	1.0	2.8	2.4	2.3	1.2	1.6
	1.2	1.3	1.0	1.8	1.8	1.3	1.9
	....	2.6	1.0	2.9	2.6	1.6	1.5
	....	1.2	1.2	3.0	2.8	1.3	1.3
	....	1.0	....	....	....	....	....
Average............	1.6	1.4		2.7		1.8	
Average*............	1.5	1.25		2.7		1.5	

*Obtained by discarding values apparently out of line

Figure 4—The potential of a titanium sample in boiling 2M hydrochloric acid as increasing amounts of copper ions were added.

Figure 5—The potential of a titanium sample in boiling 2M hydrochloric acid as increasing amounts of silver ions were added.

Figure 6—The potential of a titanium sample in boiling 2M hydrochloric acid as increasing amounts of antimony ions were added.

Figure 13

Figure 7—The potential of a titanium sample in boiling 2M hydrochloric acid as increasing amounts of nickel ions were added.

Figure 8—The potential of a titanium sample in boiling 2M hydrochloric acid as increasing amounts of gold ions were added.

Figure 9—The potential of a titanium sample in boiling 2M hydrochloric acid as increasing amounts of palladium ions were added.

Figure

Figure 10—The potential of a titanium sample in boiling 2M hydrochloric acid as increasing amounts of rhodium ions were added.
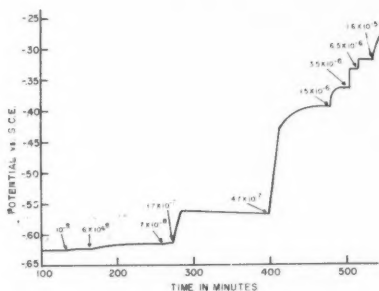
Figure 11—The potential of a titanium sample in boiling 2M hydrochloric acid as increasing amounts of platinum ions were added.

Figure 12—The potential of a titanium sample in boiling 2M hydrochloric acid as increasing amounts of iridium ions were added.

It was feared in the early phases of this work that the resistance of the external coupling might have a significant influence on the potential and hence on the corrosion rate. In order to eliminate the external resistance, the two metals were coupled directly together and the couple potential and the rate of corrosion were determined. Results of these experiments yielded the curve plotted in Figure 1. It thus appears likely that any influence of the resistance was felt both by the potential and the corrosion rate.

Potential Measurements in Acids Containing Metallic Cations

In comparing the corrosion results obtained with the titanium-second metal couples with a previous study of the effect of metallic cations on the corrosion

of titanium[1] it was observed that there were several discrepancies. As shown in Table 3, iron reduced the rate of corrosion when present as an ion and increased the corrosion rate when coupled; nickel greatly increased the rate when present as an ion and reduced the rate when coupled; silver had little effect when present as an ion but increased the rate when coupled; antimony reduced the corrosion rate to a negligible value when present as an ion and increased the rate greatly when coupled. In an attempt to resolve these apparent discrepancies, potential measurements were made on titanium samples as a function of the concentration of added ion. Results for copper, silver, antimony, nickel, gold, palladium, rhodium, platinum and iridium are summarized in Figures 4-13. A comparison of the potential values with the curve plotted in Figure 1 shows that the metal ions can have little or no effect, can activate greatly, or can inactivate the titanium depending upon the concentration.
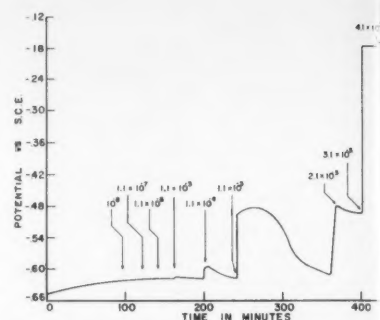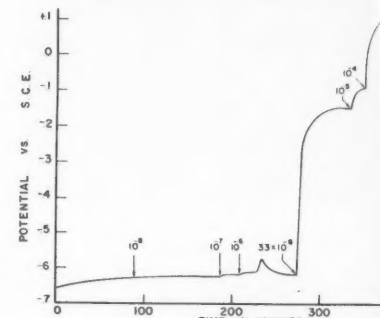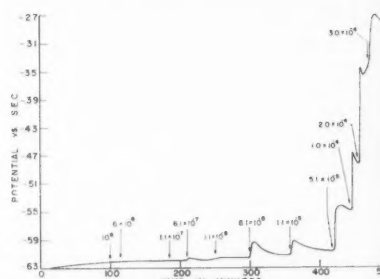
Even the platinum metals, which are such efficient inactivators for the corrosion of titanium, can increase the rate of corrosion if they are present originally as a metallic ion in the proper concentration. This fact is shown in Figure 14, redrawn from the data given in Reference 4. (The blank rate was incorrectly identified in Figure 5 in this article. As shown in Table 1, the correct blank rate for the Sample 3 titanium is 2.7 mg/cm.² 5.6 x 10⁻⁵⁹-atoms/hr. or atoms/cm.²/hr. cm.²/wa.

Long-term Exposure of Titanium to Boiling 2M HCl Containing 10⁻³M RhCl₃

It was of interest to determine how effective a platinum metal would be when originally present as an ion in solution in inhibiting the corrosion of titanium in boiling acid over a long period of time. A cylinder of titanium exposing a surface area of 5.15 cm.² was corroded for 20

5.6 x
HCl c
ment
color c
appear
becam
early
to a
solutio
and th
ment
rate c
mg./cr
1 perc
absenc

Corros
Cou
Con

It i
ability
rosion
tained
Curve
experi
the tit
num,
der o
areas
titaniu
These
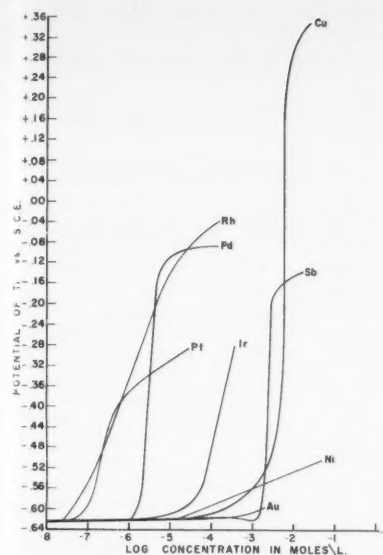
Figure 13—The effects of eight metallic cations on the potential of a titanium sample in boiling 2M hydrochloric acid.
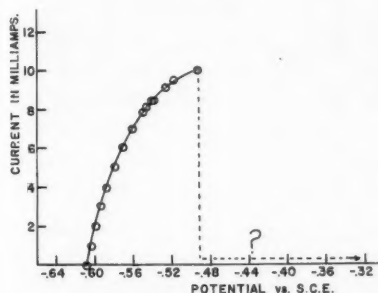
Figure 16—The polarization curve for titanium in boiling 2M hydrochloric acid.

5.6 x 10⁻⁵ 8-atoms days in boiling 2M HCl containing 10⁻³M RhCl₃. Displacement of the rhodium was slow and all color due to the Rh(III) or Rh ions disappeared after two days. The titanium became covered with a dark surface film early in the experiment, which changed to a lighter color after six days. The solution became turbid after several days and the turbidity increased as the experiment continued. The average corrosion rate during the experiment was 0.027 mg./cm²/hr. This rate is approximately 1 percent of the rate obtained in the absence of Rh(III) or Rh ions.

Corrosion of Titanium-Platinum Metal Couples in Boiling 2M HCl Containing 10⁻³M NaF.

It is well known that fluoride has the ability to increase greatly the rate of corrosion of titanium in acids. Data obtained in this study are summarized in Curve A of Figure 15. A similar set of experiments was carried out in which the titanium was coupled to either platinum, palladium, iridium or rhodium under conditions where equal surface areas of the platinum metal and the titanium were exposed to the solution. These results are summarized in Curve
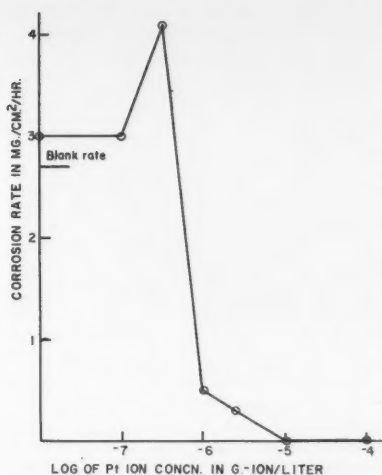
B. Two competing forces are at work in these experiments. Coupling to the platinum metal tends to reduce the rate of corrosion and the presence of fluoride tends to increase the corrosion. It will be noted that at concentrations below approximately 2.5 x 10⁻² "mole" liter of NaF, coupling to the platinum metal has the effect of decreasing the rate. The effects of the NaF and the platinum metal are cancelled at a NaF concentration of 4x10⁻³ mole/liter and the rate is same as that of the blank. At high NaF concentrations coupling to the platinum metal has no appreciable effect on the rate of corrosion.

Discussion

The results of Figure 1 are readily understandable in terms of the polarization curve of titanium in boiling 2M HCl given in Figure 16. In Figure 1 the rapid decrease in corrosion occurred at potentials above that of the titanium-antimony couple at —0.49-volt vs the saturated calomel electrode. In Figure 16 the onset of passivity occurred at potentials in excess of —0.49-volt. There is thus remarkably good agreement between the polarization curve as determined with an applied potential and the polarization curve as determined with the bimetallic couples. It was not possible to determine the polarization curve above —0.49-volt with an applied potential with the apparatus being used. The bimetallic couples, however, apparently resulted in approximately potentiostatic conditions and the onset of passivity could be followed in much the same manner as it would be potentiostatically. The curve traced out in Figure 1 is similar in shape to the polarization curve, determined potentiostatically, as presented by Cotton[5] for titanium in 40 per cent by weight sulfuric acid at 60C.

Figure 2 shows schematically the potential of the titanium-metal couple with respect to the uncoupled potentials. In Region A, represented by cadmium and aluminum, the second metal was anodic to titanium and the titanium corrosion rate was slightly decreased. In Region B,
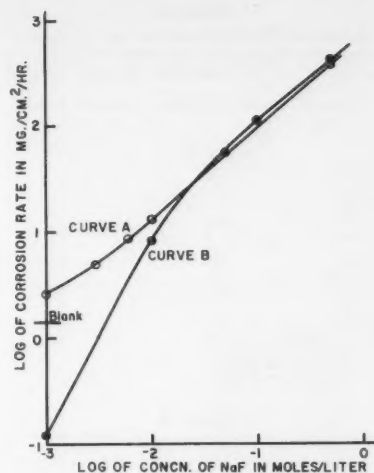
represented by tin, zirconium, lead, bismuth, and mercury, the potential was the same as that of titanium and the electrochemical corrosion was essentially under cathodic control. In Region C, represented by silver, copper, vanadium and antimony the coupled potential was intermediate to the two uncoupled potentials. In classical corrosion terms, the reaction was under mixed control. In Region D, represented by the copper-nickel alloys, iron, palladium, cobalt, nickel, gold, rhodium, platinum and iridium the potential of the couple was the same as that of the cathodic member of the couple. When coupled to any of these metals, the corrosion of the titanium was under anodic control.

The potential measurements made during the addition of metal ions to boiling 2M HCl in which titanium was corroding helped to clear up several apparent discrepancies which were discovered during the progress of this research.

Uhlig and Cobb[6] observed several years ago that copper was an efficient passivator for titanium in boiling 2M HCl when present in a concentration of 3x10⁻³M. Buck and Leidheiser[1] reported recently that a concentration of 10⁻³M copper ions increased the rate of corrosion of titanium two-fold. These apparently diverse observations are readily explained by comparison of Figures 1 and 4. It will be noted in Figure 4 that a concentration of 10⁻³M Cu(II) changed the potential of the titanium specimen to approximately —0.55-volt. This potential is characteristic of that near the maximum in corrosion rate. Increasing the concentration of copper to 5x10⁻³M caused the potential to reach +0.25-volt, characteristic of the passive region.

In the earlier publication[1] Ni ions were described as an activator for titanium corrosion whereas in the present study the coupling of titanium to nickel resulted in a decrease in the corrosion rate. Figure 7 shows that at a concentration of 10⁻³M Ni(II) the potential of titanium shifted into the active region but at

Figure 14—The corrosion of Sample 3 titanium in boiling 2M hydrochloric acid as a function of the concentration of added platinum ions.

Figure 15—The corrosion of titanium in boiling 2M hydrochloric acid containing various concentrations of NaF(A) and under the same conditions when coupled to a platinum metal (B).

TABLE 3

The Relative Effects of Metals on the Corrosion of Titanium in Boiling 2M HCl When Present as a Cation at 10^{-3}M and When Directly Coupled

(Rates of Corrosion Relative to Blank Rate)

	Metal Present as Cation* at 10^{-3}M	Metal Directly** Coupled to Titanium
Iron	0.89	1.5
Cobalt	1.3	1.1
Nickel	1.9	0.86
Copper	1.7	2.6
Silver	1.04	2.6
Cadmium	1.04	1.04
Tin	1.2	1.5
Rhodium	nil	nil
Palladium	nil	nil
Antimony	nil	2.9
Iridium	nil	nil
Platinum	nil	nil
Gold	nil	0.14
Lead	1.1	1.8

* Data from Reference 1.
** Data from Table 2.

TABLE 4

Second Metal in Titanium-Metal Couple	Region of Curve in Figure 3 in which Couple Occurs	Hydrogen Overvoltage at 10^{-3} amp./sq. cm.
Al	A	0.53[2]
Cd	A	0.99[2]
Sn	B	0.85[2]
Zr	B	0.83[3]
Pb	B	0.85[1]
Bi	B	0.69[2]
Hg	B	1.04[2]
Ag	C	0.46[2]
Cu	C	0.57[1]
Sb	C	>0.35[4]
Fe	D	0.40[2]
Pd	D	0.01[5]
Co	D	0.42[6]
Ni	D	0.32[1]
Au	D	0.17[2]
Rh	D	0.06[2]
Pt	D	0.09[1]
Ir	D	0.06[7]

higher concentrations it tended towards the passive region. Coupling of titanium to nickel was much more effective in changing the potential than a Ni(II) concentration of 3×10^{-2}M.

Antimony ions were reported to be effective in decreasing the corrosion of titanium[1] whereas in this report coupling of titanium to antimony resulted in an increased corrosion rate. Figure 6 shows that a concentration of 1.1×10^{-3}M changed the potential of the titanium specimen into the active region whereas a concentration of 4.1×10^{-3}M changed the potential into the passive region.

The metals lying on the cathodic side of the maximum in Figure 1, namely, platinum, iridium, gold, nickel, cobalt, palladium, iron and the three copper-nickel alloys are, with the exception of gold, members of the transition elements lying in Group VIII of the periodic table. The elements which have little effect or decrease the corrosion rate belong to Groups II, III and IV. This behavior is vastly different from the majority of metals[1] in which the Group VIII elements greatly increase the rate of corrosion on contact and as a general rule the elements in Groups II through V tend to decrease the rate of corrosion.

A qualitative correlation between the potential of the couple and hydrogen overvoltage can be seen in Table 4. The two elements lying in Region A, aluminum and cadmium and the five elements lying in Region B, tin, zirconium, lead, bismuth and mercury have high hydrogen overvoltages. The range extends from a low of 0.58-volt for aluminum to a high of 1.04-volt for mercury, all values being at a current density of 10^{-3} amp/sq. cm. The three elements lying in Region C, silver, copper and antimony, have intermediate hydrogen overvoltages. The elements lying in Region D, palladium, cobalt, nickel, gold, rhodium, platinum and iridium, have low hydrogen overvoltages with a maximum of 0.40-volt in the case of iron.

The remarkable effectiveness of low concentrations of the platinum metals when originally present as ions in the solution is shown in Figure 13. An appreciable change in potential and in corrosion (Figure 14) occurred when the concentration of platinum exceeded 10^{-7}M. This concentration is equivalent to a monolayer if a roughness factor of 3 is assumed and if all the platinum ions

plate out on the metal surface. It is very doubtful that the platinum would plate uniformly on the surface; it is much more logical to guess that a few small crystallites are formed. This calculation is made only to show what minute amounts of the platinum metals are necessary to change appreciably the rate of corrosion of titanium.

In the long term exposure of titanium to 10^{-3}M Rh(III) the solution became turbid and the turbidity increased as the experiment was continued. In some of the experiments in which titanium was coupled to a platinum metal, a white powder was detected at the points of contact when the two cylinders were unscrewed. X-Ray diffraction studies indicated that this white powder was TiO_2. The American Society for Testing Materials powder pattern file indicated that the best fit of the data was obtained with the card for the brookite form of titanium dioxide. These experiments, the potential experiments and the observations by many other workers suggest that the platinum metals protect the titanium because they facilitate the formation of a protective oxide film on the titanium surface.

References

(1) Bockris. *Trans. Faraday Soc.*, **43**, 417 (1947).
(2) Hickling and Salt. *Trans. Faraday Soc.*, **36**, 1226 (1940).
(3) Hackerman and Cecil. *J. Electrochem. Soc.*, **101**, 419 (1954).
(4) Centner and Straumanis, taken from summary by Akimov. *Corrosion*, **14**, 33 (1958).
(5) Hoare and Schuldiner. *J. Electrochem. Soc.*, **102**, 485 (1955).
(6) Tomashov, taken from summary by Akimov. *Corrosion*, **14**, 33 (1958).
(7) Estimated from data of Newbery. *J. Chem. Soc.*, **109**, 1051, 1107 (1916).

1. W. Roger Buck III and Henry Leidheiser, Jr. *Corrosion*, **14**, 308 (1958).
2. W. Roger Buck III and Henry Leidheiser, Jr. *Nature*, **181**, 1681 (1958).
3. N. D. Tomashov. *Corrosion*, **14**, 229 (1958).
4. W. Roger Buck, III and Henry Leidheiser, Jr. *Zeit, fur Elektrochem.*, in press.
5. J. B. Cotton. *Chem. and Ind.*, 1958, 68.
6. J. R. Cobb and H. H. Uhlig. *J. Electrochem Soc.*, **99**, 13 (1952).

Instruments for Measurements in Underground Corrosion Work*

By K. G. COMPTON

Figure 1—D'Arsonval movement.

Abstract

Instruments commonly used for measuring electrical currents and potentials associated with corrosion of underground structures are described and their circuits explained. Considered are voltmeters, various kinds of potentiometer voltmeters and electrodes. Limitations of accuracy and fundamental principles of the use of instruments are given.

Measurements described include resistivity and resistance, and special measurements, such as polarization current. Function and characteristics of combination instruments are described. Instruments are illustrated and schematic circuit diagrams given. 2.4.2

About the Author

K. G. COMPTON has worked with corrosion problems for more than 25 years at the Bell Telephone Laboratories, Murray Hill, N. J. During World War II he was a consultant on the deterioration of materials to the NDRC and the Chief of Ordinance; he has also been active on corrosion committees of several technical societies. He received his training in electrical and chemical engineering and in electrochemistry at the State College of Washington.

THE MEASUREMENT of the electrical potentials and currents associated with the corrosion of underground structures is an important part of its study and mitigation. Many instruments are available for these measurements and it is important that corrosion engineers keep themselves informed on their uses and limitations. The exactness or precision with which measurement may be made depends upon many factors, some of which are beyond the control of the engineer. In selecting instruments for the job he must weigh the factors subject to his control and make compromises with a clear understanding of their effect on his results.

Voltage Measurement

The most common type of instrument used in corrosion studies is the moving coil deflection voltmeter. This is actually a microammeter with resistors in series with the coil to give the proper deflections corresponding to the scale required. The current through the coil causes the deflection and the torque is a function of the product of the current and the number of turns in the coil. If the number of turns is increased with an accompanying decrease in wire size, smaller currents will produce equal torques. However, the resistance of the coil will have increased and therefore require more voltage to produce the current.

The sensitivity of the instrument is the minimum electrical energy which will cause a readable deflection of the pointer. However, makers of moving coil voltmeters use an indirect expression, ohms per volt, to indicate current sensitivity. The higher the ohms per volt, the smaller is the current which will produce the deflection. Other expressions for sensitivity are sometimes used, such as millimeters per volt, microamperes per division or microwatts for full scale deflection. Similarly, a practice has developed of referring to the accuracy of an instrument as a percentage of the full scale deflection. Thus at a full scale deflection, the accuracy may be $\pm \frac{1}{2}$ of 1%, but drops to $\pm 2\%$ at quarter scale and $\pm 5\%$ at tenth scale deflections. The movement of a typical moving coil permanent magnet instrument is
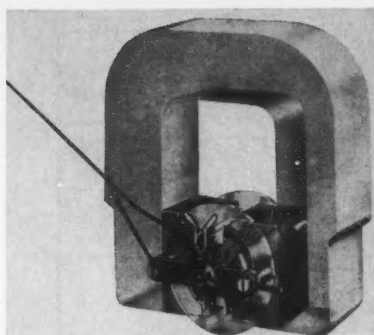
shown in Figure 1. The coils usually are mounted on steel pivots riding in jeweled bearings. However, a newly developed diamond pivot has appeared on the market which is said to greatly increase the ruggedness of the instruments.

Another type of instrument for measuring potentials is the potentiometer voltmeter shown in Figure 2. The slide wire bridging the battery is adjusted until the galvanometer reads zero. The potential indicated on the voltmeter is equal to the unknown potential. Because only a very small part of the current needed to give a full scale deflection of the galvanometer is required to indicate deviations from zero, this instrument may be said to have a much higher sensitivity than its counterpart in the simple voltmeter. Therefore, less error is introduced from the IR drop of the measuring current flowing through external circuit resistance, an error that can be very significant if this resistance is large. In Table 1 is given the effect of external circuit resistance on readings of simple deflecting voltmeters and a potentiometer-voltmeter having a galvanometer element with a sensitivity of 50,000 ohms per volt and a coil resistance of 1500 ohms. Absolute accuracy of scale is assumed in this Table for all voltmeters and the precision of balance of the galvanometer element is $\pm 1\%$ (actually, this could be reduced to nearly $\pm .1\%$).

An example of a simple potentiometer-voltmeter, similar to that described above is shown in Figures 3 and 4. The schematic diagram D shows the switching arrangement that permits the meter to be used as a simple voltmeter A, as the galvanometer B and as the voltmeter of the potentiometer-voltmeter C. The slide wire is adjusted (B) until there is no needle deflection. The meter is

Figure 2—Basic potentiometer-voltmeter circuit.

switched to (C) to read the unknown voltage. The switch that open-circuits the battery is part of the key and is open in the key's mid position. Push buttons were found to be more satisfactory than rotary switches for selecting ranges.

The slide wire potentiometer in which

TABLE 1—Error Produced by External Resistance

External Series Resistance Ohms	Precision of Galv. Balance Mv. %	Approx. Error (% of 1 v full scale)			
			Voltmeter Sensitivity Ohms per Volt		
		Pot Vm	50K	200K	500K
0	± .3	± .03	0	0	0
3500	1	.1	6.5	1.5	.5
8500	2	.2	14	4	1.5
50,000	10.3	1	50	20	9
100,000	20.3	2	66.7	33.3	16
500,000	100	10	90	71	50
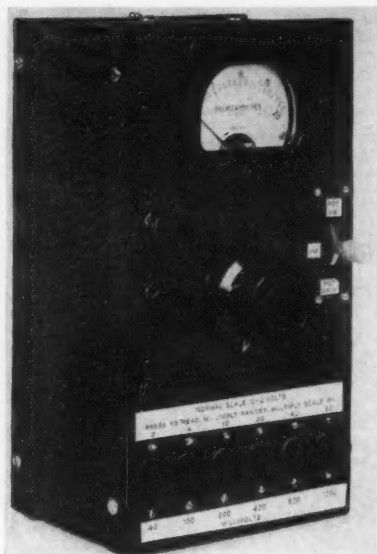
Figure 3—A simple and practical potentiometer-voltmeter for corrosion tests.

Figure 4—Schematic circuitry of the instrument shown in Figure 3.

the drop along a slide wire is calibrated against a standard cell provides a means of obtaining a higher precision than with deflecting indicating instruments. While the portable models have been used in the field with some success, they are rather slow in operation and are useless in the presence of fluctuating potentials. The circuit diagram of a commercially available potentiometer is shown in Figure 5. The accuracy of this instrument is ± 0.05% of the first dial reading when the external resistance is sufficiently low. For a reading of 0.6252 the precision would be ± 0.3 millivolts, which is more than ten times better than any portable deflection voltmeter. External resistance reduces the sensitivity but does not introduce a direct error.

A relatively new instrument, as far as

the commercial market is concerned, is the portable dc vacuum tube voltmeter or electrometer. This instrument permits reasonably accurate measurements of potentials through very high external resistance because the current required to operate it is of the order of 10^{-14} amperes. In the field, this high "sensitivity" cannot be used because static disturbances will produce errors. However, it will permit measurements in circuits where other devices are inoperative. A zero drift which is encountered in the low ranges and when the instrument is first activated, must be considered, but this is not a very significant handicap, considering its other advantages. One such instrument is shown in Figures 6 and 7 and another in Figure 8. Disregarding drift, the accuracy of these instruments is about ± 2% of the full scale reading.

Another instrument which was devised to minimize the effects of external circuit series resistance is the dual sensitivity voltmeter shown in Figure 9. If the second reading, obtained by pushing the button, is lower than the first, a series resistance is indicated. If not, the reading is accurate to 1% of the full scale value. If the difference is less than 5%, adding the difference to the first reading brings the accuracy to within 2%. If the difference is greater than 5%, the true value can be calculated to within 2% from the formula,

$$V_o = V_1 \frac{1}{1 - \dfrac{(V_1 - V_2)}{V_2}}$$

Figure 5—Schematic circuit of commercial portable null potentiometer.

The writer has discussed the basic accuracy of these voltage measuring devices and the effect of the series resistance in the external circuit as a source of error. It must be pointed out that the most precise and sensitive instruments will not overcome the errors due to IR drop in the earth or other medium, be-

Figure 8—Vacuum tube millivoltmeter (dc.).

tween
struct
meter
extern
the s
readin
is hig
deflec
series
tion n

A r
pin, a
the s
shown
is pla
per su
ous b
the o
fairly
exists
tion i
to di
Thus
tact i
of th
other
tentia
poten
able,
ignore
but b
rectly
braic
Chan
for th
ponen

Sev
are a
trodes
cell, t
ride o
a stan
sion e
one m
age,
nance
be of
sitive
erence
mel c
measu
may
cell.

Figure 6—Vacuum tube voltmeter (dc.).

Figure 7—Schematic circuit of instrument shown in Figure 6.

Figure 9—Dual sensitivity voltmeter.

Figure 10—Circuit in measuring structure-to-earth to half cell potentials.

Figure 11—Basic "zero resistance" ammeter circuit.

Figure 12—Electronic galvanometer (dc).

tween the reference electrode and the structure, which are not the result of meter current. The presence of a high external resistance may be detected with the simple voltmeter by observing the reading on two ranges. If the reading is higher on the higher range (smaller deflection and hence smaller current) series resistance is present and a correction must be made.

Reference Electrodes

A reference electrode may be a steel pin, a lead slug or a half cell such as the saturated copper sulfate electrode shown in Figure 10. A piece of copper is placed in a saturated solution of copper sulfate in a container having a porous bottom. The potential E_1 between the copper and the solution remains fairly constant. A small potential E_2 exists between the copper sulfate solution in the porous plug and the soil due to differences in ionic concentrations. Thus a relatively constant voltage contact is made to the earth. E_2 is made up of the IR drops mentioned above and other liquid junction concentration potentials. E_3 is a metal-to-metal contact potential which is not readily measureable, is relatively constant and can be ignored. E_4 is the significant potential, but because it cannot be measured directly, E must be considered the algebraic sum of the other potentials. Changes in E_4 are reflected in E except for the above mentioned IR drop component of E_3.

Several commercial sources of supply are available for various reference electrodes such as the copper sulfate half cell, the calomel cell and the lead chloride cell. The first of these has become a standard for field use by most corrosion engineers. In selecting the half cell, one must be mindful of electrolyte leakage, convenience and ease of maintenance. The resistance of the cell may be of some concern where the less sensitive meters are used. Of the three reference electrodes mentioned, the calomel cell provides the most reproducible measurements. Either of the other two may vary several millivolts from cell to cell. Consequently when measurements
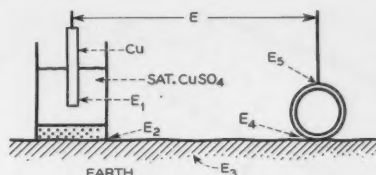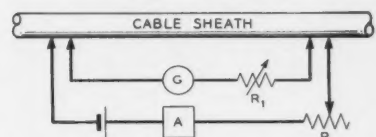
are made between two cells in contact with soil the difference may be considerably greater due to variations in E_2 and E_3.

Current Measurement

Currents can be measured by simple moving coil ammeters and milliammeters where these can be inserted in the circuit. Their accuracy limitations are the same as those in voltmeters. In some instances, measurements of the current flowing in a pipe, cable, or a bond wire may be required where the meter cannot be inserted in the circuit or where the resistance of the instrument would affect the results. Here the so-called "zero resistance ammeter" circuit is brought into play. In Figure 11, a galvanometer or other low voltage potential measuring device is bridged across a section of cable or pipe, or a length of bond wire. An ammeter, a battery and a resistor are connected as shown. If the resistor R is adjusted until G reads zero on its most sensitive scale, the current formerly in the bridged section will have been diverted through the ammeter where it can be measured.

In the case of full sized cable sheaths, the resistance of a short length of sheath is a fraction of a milliohm. Hence, the measurement of currents of the order of one milliampere requires that the galvanometer be sensitive to fractions of a micro-volt. Several sensitive devices are on the market, such as that shown in Figure 12. Low voltage direct current is fed through a filter, to eliminate ac, into a chopper and the windings of a step-up transformer where it is converted into ac. This is amplified, rectified and passed through a moving coil galvanometer which is the indicating instrument. Usually diode current limiters are provided to protect the galvanometer. The writer has such a device that will detect a 1-milliampere current in a full sized sheath (.0001 ohm per foot) with a 2-foot span between contacts. In making measurements of this sensitivity, care must be exercised to avoid errors due to thermoelectric effects. The author uses lead coated wires for the potential leads when making measurements on cable sheath. Other "zero-resistance ammeters" have been described in the literature or are available on the market.
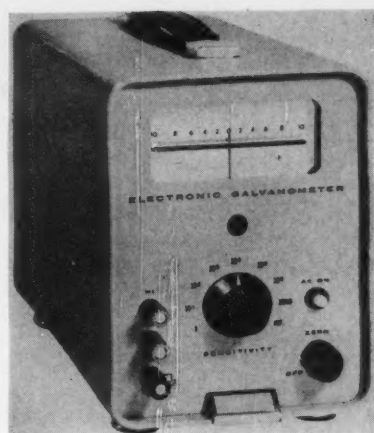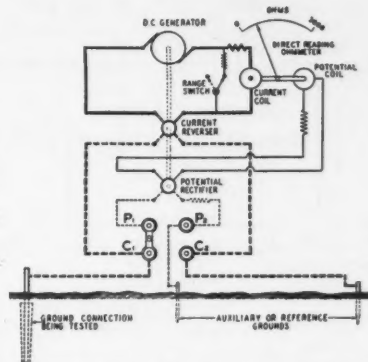
Figure 13—Circuit of instrument for measuring soil resistivity.
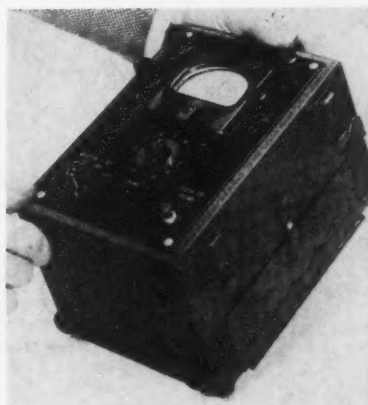
Figure 14—Instrument for measuring resistivity.
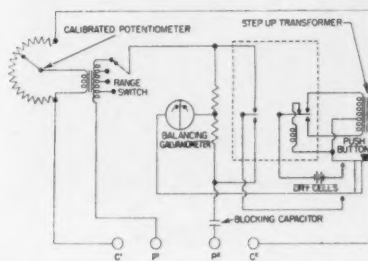
Figure 15—Schematic circuit of instrument in Figure 14.

Figure 16—Shepard's cane.

NULL BRIDGE FOR MEASURING
CABLE-TO-EARTH POTENTIALS

EQUIVALENT BRIDGE CIRCUIT

COMMON SHAFT SO ONE RESISTANCE
DECREASES WHEN THE OTHER IS INCREASING
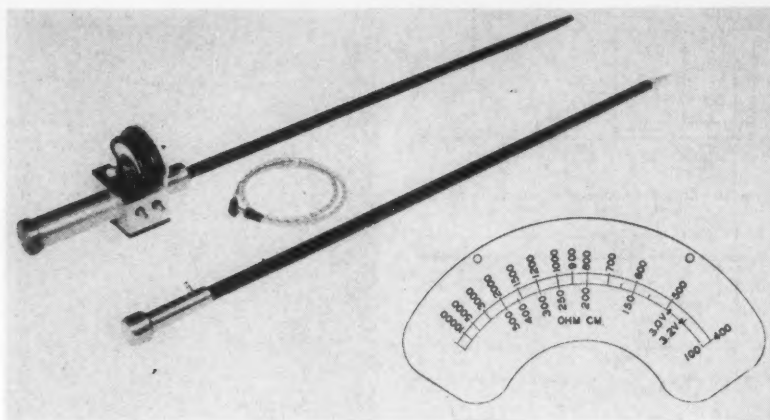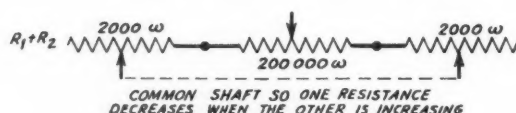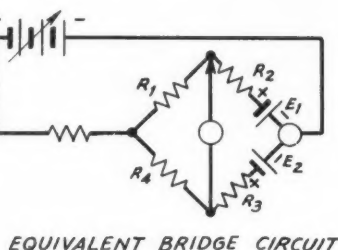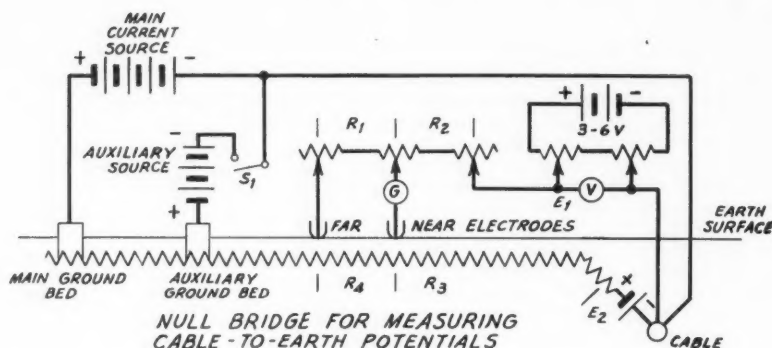
Figure 17—Pearson bridge.
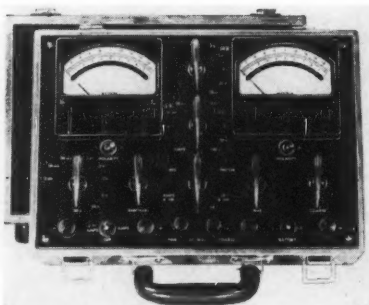
Figure 18—Multiple combination meter to balance
a variety of tests.

Resistivity and Resistance Measurements

Measurements of the resistivity of the soil, the resistance between structures or of structure to earth are often important in underground corrosion work. An ohmmeter or the fall-of-potential method with an ammeter and a voltmeter may be used, but other instruments are more satisfactory. The circuit of one of these is shown in Figure 13, and a model of another and its circuit are shown in Figures 14 and 15. Because a high degree of precision usually is not required the accuracy of most of the instruments used for these measurements is satisfactory. The way the instruments are used may introduce errors of greater magnitude than those inherent in the instruments themselves. The Shepard Cane shown in Figure 16 was developed at the Bureau of Standards to permit rapid surveys of earth resistivity near the surface. The instruments shown in Figures 14 and 15, using the four pin method, permit measurements of resistivity to considerable depths.

Special Measurements

In some instances it may be desired to eliminate from the measurement as much of the IR drop in the earth as possible when adjusting a cathodic protection system. For this purpose various "bridge" circuits have been devised. The most satisfactory is that proposed by Pearson and developed by Hadley and Logan. The circuit is shown in Figure 17. The vacuum tube electrometer shown in Figure 6 is an ideal instrument for use as a galvanometer in this circuit. With the circuit set up as shown, the current passing through the earth to the structure is varied in small increments by small changes in either the main source or in an auxiliary source, and the ratio of R_1 to R_2 is varied until changes in current produce no change in the deflection of the galvanometer. The potentiometer voltmeter section is adjusted until the galvanometer reads zero. Under these conditions the reading of E_1 is independent of IR drop produced by the current from the ground bed and is equal to E_2. (This is true, provided there are no stray fields between the far electrode and the structure.)

This Pearson Null Bridge has been used successfully in determining the current required to polarize underground structures to the point of incipient hydrogen evolution. After the bridge is balanced, the protection current is increased from a very low value in successive increments and the potential determined for each value of current. Potential is plotted against the log of the current, and the "knee" of the curve is taken as the point at which protection is achieved. A discussion of this method has appeared in several papers.

Combination Instruments

Where a variety of measurements may be required, the corrosion engineer might find it desirable to equip himself with one of the combination test sets such as the excellent units shown in Figure 18. These sets provide in one case a low resistance millivolt-voltmeter, a high resistance voltmeter, a potentiometer voltmeter, a milliammeter, ammeter, a zero-resistance ammeter, a bias voltage, as well as internal batteries, controls and rheostats for providing small test currents. The model used in the writer's laboratory, in addition to the items listed above, contains a vacuum tube voltmeter with ranges of .1 to 10 volts and a provision for self-calibration. These sets are quite rugged and were designed by a practical corrosion engineer. The manufacturer supplies a complete set of illustrated instructions on the use of the set for making a wide variety of corrosion measurements.

As can be seen from the previous dis-

cussion, there are many factors other than first cost which influence the selection of instruments such as ruggedness, portability, sensitivity, period and precision. Where the instrument is subject to rough handling by field crews, ruggedness is of paramount importance. Where structure-to-soil potentials are being measured in high resistivity earth, sensitivity is important. The greater the precision and the more delicate the instrument becomes, the more skilled and careful the operator must be. It is surprising and disheartening to find many engineers in the field sometimes making measurements incorrectly with the result that much of their data is almost worthless. There is a need for a better understanding of the characteristics of instruments and their correct use.

In measuring the potential of a structure to the soil in contact with it, one is interested only in the potential at the soil-structure interface. Because this cannot be measured directly, one must measure the difference between this potential and some reference electrode in contact with the earth. The IR drop in the soil between the structure-soil interface and the reference electrode, whether produced by a cathodic protection current or a stray current, will cause a considerable error in the potential reading, hence the shorter the path between structure and half cell, the better. The IR drop error due to the current drawn by the measuring device, can best be eliminated by using a potentiometer voltmeter or vacuum tube voltmeter. Where fluctuating potentials are encountered, a short period instrument is required. Some high resistance voltmeters are adequate in this respect as are the vacuum tube voltmeters, but potentiometer devices are useless.

Current in cable sheaths or pipes is best measured by the zero resistance ammeter method, even though the sensitivity of the galvanometer element is low. Usually, the current passing between tructures in a bond can be measured with an ordinary ammeter. If the resistance of the meter influences the reading, again the zero resistance ammeter should be employed. As a rule, the ammeters and milliammeters available for corrosion measurements are sufficiently rugged for field use.

Auxiliary equipment such as reels, probes, communication sets, pipe locators and current interrupters are essential but vary from job to job and will not be discussed here. Neither will recording meters be discussed because their development is in a state of flux. Several new models on the market have not been used long enough to work out the "bugs." Some older models are relatively rugged but are of little use because their sensitivity is too low. At least two manufacturers have portable recorders that give promise of providing adequate sensitivity when the driving motors and rate of response are improved.

Oftentimes at meetings of corrosion engineers a question is raised by some individual as to what meter to use to get an accuracy of $\frac{1}{2}$ of 1%. In the discussion that follows, it becomes apparent that many of the others present are equaly lacking in an understanding of the fundamentals of electrical measurements in corrosion. The engineer must first know the characteristics of the instruments at his disposal, then the external circuitry of the things he is trying to measure. So armed, he can make an intelligent appraisal of the reliability of his data and plan the most practical solution to his corrosion problem.

Any discussion of this article not published above will appear in the June, 1960 issue

Equivalent Electrical Circuit Analogy Of Structure-to-Soil Potentials*

By ROY O. DEAN

Abstract

Data obtained from structure-to-soil potential measurements, even when made with extreme care and precision, sometimes appear to be erratic and anomalous.

The "electrical equivalent circuit" analogy is very helpful in understanding and analyzing these measurements; it explains why the placement of the reference electrode is sometimes unimportant while at other times it may be very critical and why the measurement of structure-to-soil potentials cannot be considered an indication of interference unless properly evaluated in connection with all associated factors.   2.3.5

S TRUCTURE-to-soil potential measurements are now generally accepted by most corrosion engineers as one of the methods of obtaining data in connection with cathodic protection and cathodic interference problems. These potential measurements, even when made with extreme care and precision, often appear erratic and erroneous.

Interpreting the meaning of these potential measurements has probably been the most confusing, controversial, and the least understood factor the field engineer has encountered in attempting to analyze his test data. This lack of understanding may be largely responsible for the delay of the profession in establishing standards or uniform methods and practices for determining cathodic protection and resolving interference problems.

A recent government publication[1] which includes actual case histories obtained from the answers to questionnaires sent to industry, clearly indicates the absence of any standard concept, uniformity of measurement methods or interpretation of tests. Similar conclusions can be reached from answers to questionnaires sent out by NACE T-4 committee in 1948 and by the American Gas Association in 1953.

There have been many attempts to develop an application of basic "Structure to Soil Potential" measurements which would be simple, yet valid and authentic. One approach used by Brown and English[2] to explain the electrochemical principles of cathodic protection was the "equivalent electrical circuit"; and it would appear that this same analogy may be of value in analyzing and interpreting other structure potential data. This paper submits concepts and examples of practical applications of the "equivalent electrical circuit" which are believed to be useful in the gathering of data and its interpretation when evaluating cathodic protection or investigating interference problems encountered in field engineering. Some data, which otherwise appear to be meaningless or even spurious, then become understandable and logical.

The circuits presented in this paper are purposely made basic in order to illustrate a few of the simple cathodic protection and corrosion circuits. Many other more complex "Equivalent Circuits" necessarily would be required in order to represent all of the conditions found in actual field practices.

Figure 1A shows a simple underground structure with a galvanic cell. Current Ia leaves the anode and enters the earth.

Current Ic enters the structure at the cathode and returns through the structure to the anode. In this case Ia = Ic.

Figure IB shows this same simple galvanic cell as an "equivalent electrical circuit" and with its other associated electrical components. In addition to the current Ia and Ic, it is also possible to indicate the voltage Ea of the anode and the voltage Ec of the cathode, the resistances Ra at the anode and Rc at the cathode, and the resistance Rs of the structure itself. Resistances Ra and Rc are the total of all resistances at the anode and at the cathode and therefore will include the resistance of any coatings, oxides, films, polarization, anode or cathode-to-soil contact and all of the soil resistance which is associated with the anode or cathode current.

When measuring structure-to-earth potentials at the anode, utilizing a copper-copper sulfate reference electrode, there will be included a voltage drop due to the current Ia through the resistance Ra. If the current Ia is of sufficient magnitude to measure, the measured potential will decrease as the copper sulfate electrode is moved away from the structure and additional increments of the significant soil resistance, portion of resistance Ra, are included in the circuit.

When measuring similar structure-to-earth potentials at the cathode, the potential measured will include the voltage drop due to the current Ic through the resistance Rc. However, the polarity of this voltage drop will be in the opposite direction to that at the anode. The measured potential at the cathode will increase as the copper sulfate electrode is moved away from the structure and additional increments of the significant soil resistance, portion of the resistance Rc, are included in the circuit.

At some distance from the structure at both the anode and the cathode, no additional significant voltage drop will be measurable as the reference electrode is moved farther away from the structure. The point beyond which no change in potential is measurable, then can be concluded to be the end of the resistance Ra and Rc for this particular circuit and this current value.

Figure 2A shows a typical curve of potential versus distance that will be measured at an anode, when the current Ia is of sufficient magnitude to cause a measurable voltage drop through the "soil-resistance component" of the resistance Ra. At the anode the measured voltage decreases in magnitude as the reference electrode is moved away from the structure.

About the Author

ROY O. DEAN is supervisor of the Corrosion Engineering Department in the Bureau of Tests and Inspection, Pacific Gas and Electric Co., Emeryville, Cal. He received a BS in electrical engineering from Tri-State College and is registered in California as a professional engineer. He has been a member of NACE since its formation.
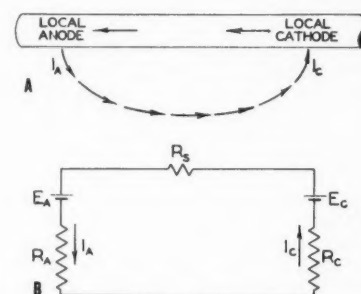
Figure 1—Simple underground structure with galvanic cell (A) and analogous circuit (B).
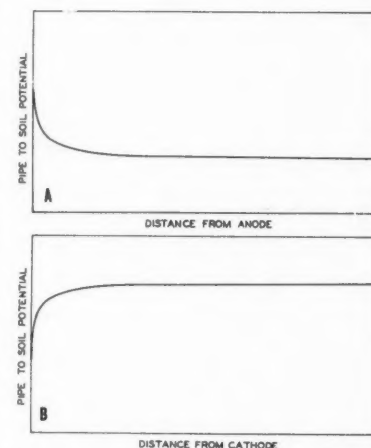

Figure 2—Typical curves potential versus distance, at anode (A) and at a cathode (B).
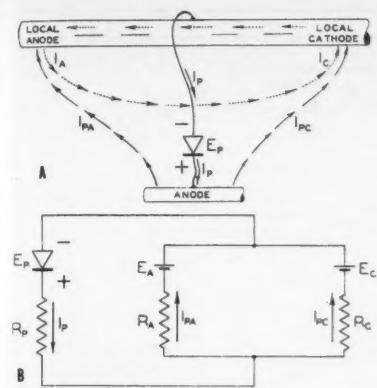
Figure 3—Schematic layout of cathodic protection system (A) and analogous electrical circuit (B).

Figure 2B shows a typical curve of potential versus distance that will be measured at a cathode, when the current Ic is of sufficient magnitude to cause a measurable voltage drop through the "soil-resistance component" of the resistance Rc. At the cathode the measured voltage increases in magnitude as the reference electrode is moved away from the structure.

The measurement of the voltage drop across a portion of the soil resistance comprises the basic operating principle of the McCollum Earth Current Meter, but often seems to be completely ignored by many when making structure-to-soil potential measurements.

Many local micro-galvanic cells on underground structures are not of sufficient magnitude either to be located or to have their potentials measured from the surface of the ground with a copper sulfate electrode. However, cathodic protection currents and significant interference currents can be so measured.

Figure 3A shows the same anode and cathode currents Ia and Ic as a dotted line. Cathodic protection then is applied to the underground structure by means of a rectifier and anode bed. Cathodic protection current Ip then flows from the cathodic station anode bed to both the local anode and local cathode, therefore both are now cathodes, as shown by the dashed lines.

Figure 3B below is the "equivalent electrical circuit" of the application of cathodic protection to the local anode and cathode circuit previously shown. A cathodic protection circuit has been added with the rectifier voltage Ep and protection current Ip passing through the total ground bed resistance Rp. A portion of the protective current Ip will flow through the resistance Ra to the former local anode. This value of protective current will be designated Ipa. Another portion of the protective current Ip will flow through resistance Rc to the former local cathode and will be designated as Ipc. Ipa + Ipc = Ip. The resistance Rp of the cathodic protection anode is the total of all resistance associated with the anode and will include the resistance of any coating, oxides or films on the anode, anode-to-soil contact and the resistance of the earth itself away
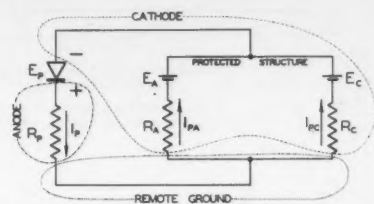

Figure 4—Equivalent circuit divided into rectifier anode, cathode and remote ground sections.

from the anode to a point where no additional significant voltage drop is measurable, i.e., "remote ground."

Figure 4 shows this same equivalent circuit divided into three component parts, rectifier anode, cathode and remote ground.

When measuring structure-to-earth potentials, if the copper sulfate electrode is placed in the anode field, there will be a decrease in potential as the electrode is moved farther away from the anode and increments of the resistance Rp are added to the circuit; until all the resistance Rp is included. Beyond this point no additional decrease in potential will be observed. It can be seen readily that these changes in potential readings have no relationship to the actual potential of the structure and that the electrode should be placed at remote ground as far as the anode is concerned.

The voltage drop due to the cathodic protection currents Ipa and Ipc flowing through the resistance Ra and Rc will be indicated when the copper sulfate electrode is placed in either of the fields which are now cathodes. This voltage drop will indicate an increase in potential as the reference electrode is moved farther away from the structure, until all of the resistance either Ra or Rc has been included in the circuit. Beyond this point no additional increase in potential will be observed.

Remote ground may be defined then, as any place beyond which no additional significant voltage drop from either the anode or cathode circuit resistance of the structure is measurable; and also remote from all anodic and cathodic fields of foreign structures.

Figure 5A shows the potential profile obtained at an anode when the protected structure was a very well-coated line. The reference electrode was first placed at 1-inch intervals from the anode for a distance of one foot, then at 1-foot intervals up to 12 feet. Note the rapid change of potential in the first foot, the change being particularly abrupt within the first few inches.

Figure 5B below is the same anode field with potentials measured at 100 foot intervals to a distance of 1200 feet. No additional decrease in potential was observed beyond 1100 feet, which therefore would be considered remote ground at this particular location and for this specific current output. The distance to the remote ground of an anode field will vary with soil resistance, current output and from the influence of numerous physical factors, from only a few feet to 2000 feet or more. From this it may be concluded
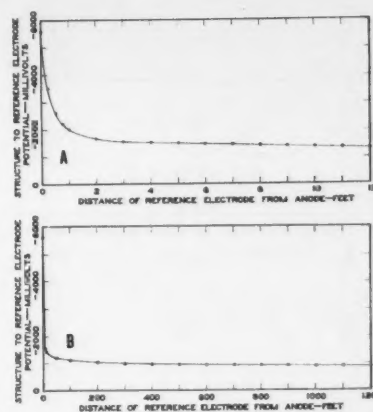
Figure 5—Potential profile on a very well-coated line (A) and measurements at 100-foot intervals of same anode field (B).
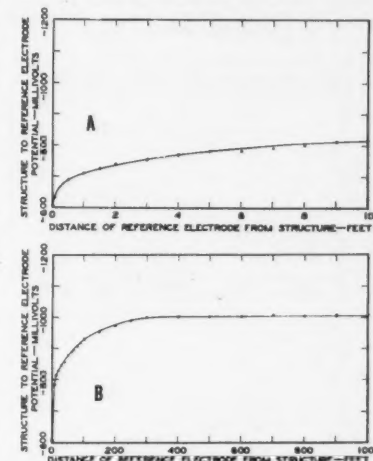
Figure 6—Potential profile measured in a cathode field (A) of poorly-coated section of otherwise well-coated line and measurements at 100-foot intervals of same field (B).

that any number of structure-to-soil potentials varying considerably in value could be measured, depending upon where the electrode was placed in the anode field.

Figure 6A shows the potential profile measured in a cathode field due to a poorly coated section of an otherwise well-coated line. The readings were taken with the reference electrode placed at 1-inch intervals away from the structure for a distance of 1-foot, and then at 1-foot intervals up to 10 feet. Note here again, the sharpest increase in potential was observed in the first few inches away from the cathode.

Figure 6B below shows this same cathode field with potentials measured at 100-foot intervals to a distance of 1000 feet. No additional increase in potential was observed beyond 300 feet, which would be considered remote ground at this particular location and current value. From this too, it may be concluded that any number of structure-to-soil potentials, varying considerably in value, could be measured depending upon just where the electrode was placed in the cathode field.
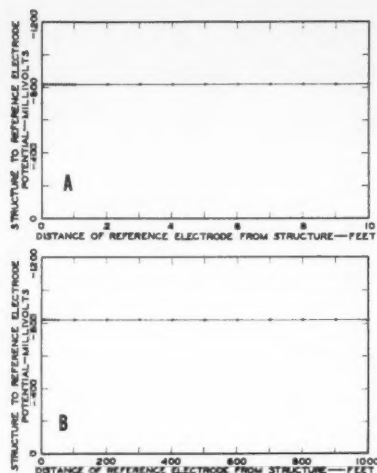
Figure 7—Potential profiles of potential versus dis-tance measured in cathodic field on well-coated, cathodically protected line.

Figure 8—Anode and cathode field widely separated (A) and anode and cathode field adjacent (B).

Figure 9—Saw tooth profile (A) may result from measurements made with reference electrode in anode or cathode field. Detailed investigation of profile peak B (B) and detailed investigation of profile peak C (C).

Figures 7A and 7B show profiles of potential versus distance measured in a cathode field on a very well-coated, ca-thodically protected gas line. This is a perfectly straight line from inches away up to 1000 feet which would indicate all locations are "remote." Referring back to the "equivalent electrical circuit" it is seen that although resistance of the cathode circuit still exists, no voltage drop in the soil is measurable because the cur-rent flow is minute. All voltage drop and the significant portion of the cathode re-sistance is concentrated at the coating interface.

Figure 8A shows both an anode and cathode field widely separated, with re-mote ground extending for a considerable distance in between, while Figure 8B shows an anode and cathode field adja-cent to each other, with no specific re-mote ground between the two fields. Although both figures are plotted from data obtained in actual field measure-ments where the conditions were specially prepared for these tests it would be pos-

sible for these conditions to actually exist. All of the other curves shown are from actual field data as obtained, and a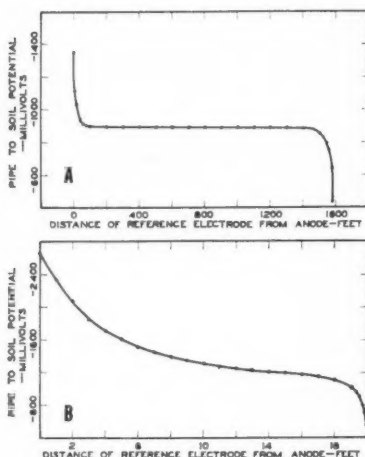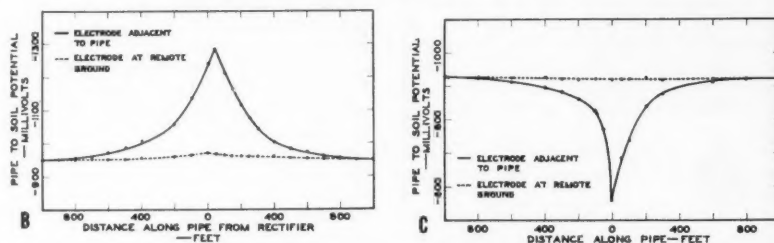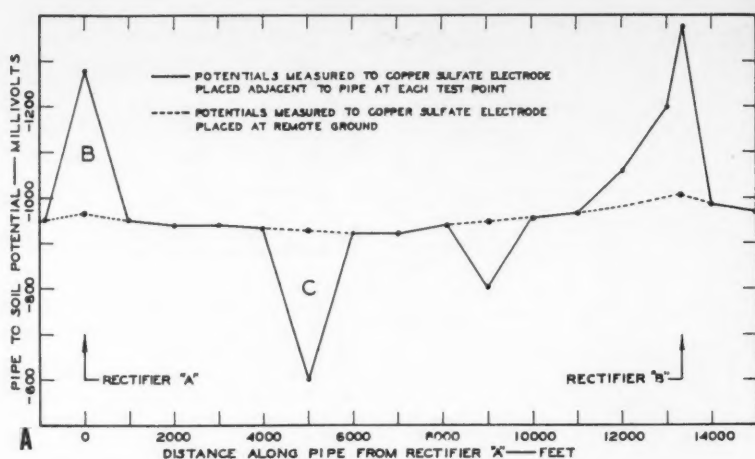re typical of a great number which we have made in the past several years. To better understand the relationship of test data, it is helpful to always think of a separate and distinct anode and cathode field. Figure 8A shows them separate while in Figure 8B there is no distinct separation.

Remote ground, however, can be de-termined in the field by making a po-tential versus distance profile away from the structure. In addition, complete knowledge of all other underground structures and assurance by test that the reference electrode is in neither an anode or cathode field of these other structures is necessary.

To facilitate the location of remote ground, a corrosion engineer in Southern California has devised and patented a copper sulfate electrode wheel which can be rolled along on the surface of the ground.

When structure-to-soil potentials meas-ured along a pipe line under cathodic protection are plotted and appear as a "saw tooth" profile, as shown in Figure 9A, additional investigations may show some of these measurements were made with the reference electrode in the anode or the cathode field. When the reference electrode is remote, the "saw tooth" por-tion of the profile will then appear as shown by the dotted line.

Figures 9B and 9C show a more de-tailed investigation of the peaks B and C of Figure 9A. Figure 9B shows an anode field where the potentials were measured at a number of locations both adjacent

and remote. The potential drop measured between the various points on the struc-ture, due to the current flow in the struc-ture, checks very closely with the difference in structure-to-soil potentials measured to remote ground at these same points, but does not check with those measured when the reference electrode is placed adjacent to the structure. By plac-ing the reference electrode at the "remote ground" location, any variability in the measurements which would be introduced by placement in an anodic or cathodic field, is completely excluded. Accordingly, this substantiates the conclusion that po-tentials measured to the remote ground location are reliable and authentic.

It would appear then that if the refer-ence electrode is placed in the anode field, the effectiveness of "hot spot" pro-tection may be misinterpreted and its value over-estimated.

Figure 9C shows a relatively concen-trated cathodic field. These curves are plotted from data obtained at a field asphalt-swabbed valve in an otherwise well wrapped gas line. The soil potentials were measured in both directions away from the valve and were measured to both adjacent and remote reference elec-trodes. Here too, the potential drop be-tween the various points on the pipe check very closely with the difference in the potentials measured to the remote electrode but do not check with the dif-ferences in potential indicated with the electrode adjacent to the pipe.

Previously defined "remote electrode potential" measurements provide a valid and reproducible potential of the struc-ture. Since this is true, average values
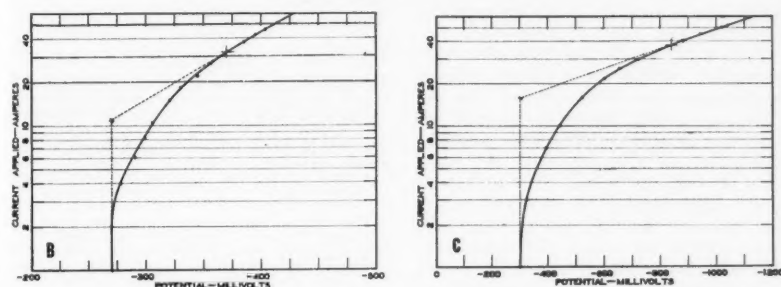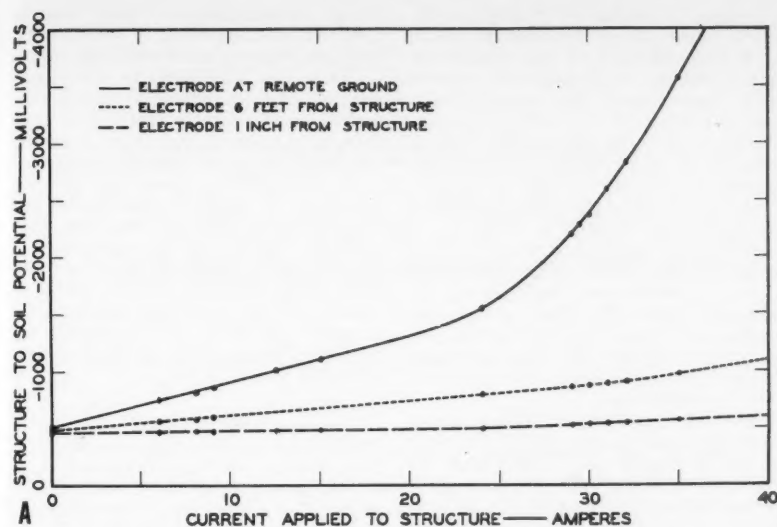
Figure 10—Profile potential-versus-current curves on parallel interconnected almost bare penstocks (A). Results of Pearson Null Circuit Potential Break Curve (B) and Modified Null Break Curve (C) on the same penstocks.

Figure 11—Schematic layout structure under cathodic protection with unprotected structure in vicinity (A). Equivalent electrical circuit of this layout (B).

Figure 12—Layout of cathodically protected well-wrapped line passing under three bare lines also under protection (A). Potential Profile both ways from crossing (B).

of a current flow on a structure between any two measured points may be calculated when the resistance of the structure is known by using the difference in remote potentials at these points.

Figure 10A shows potential-versus-current curves which were obtained on two parallel interconnected almost bare 6-foot diameter steel penstocks. Initial or static potentials measured to a reference electrode one inch, six feet, and 1100 feet away from the penstocks with zero current before any polarization occurred, indicated an earth current discharge. All values of applied protection indicate an earth current flow to the pipe. A cathodic current of 185 amperes would be required to achieve a potential of 850 millivolts at the electrode placed at a distance of one inch (the lower curve), 30 amperes with the electrode spaced six feet (center curve and 9 amperes when the electrode is at the remote location (upper curve).

Figures 10B and 10C show the results of the Pearson Null Circuit Potential Break Curve and the Modified Null Break Curve obtained on the same penstocks. The Pearson Null Break indicates a protection current requirement of 11 amperes, while the break in the Modified Null indicates that a current of 16 amperes is required. If the tangential points of these potential break curves are used as the criteria for protective current, the

Pearson Null Break indicates that a value of 32 amperes is necessary; whereas the Modified Null shows that 36 amperes should be applied.

An understanding of the "electrical equivalent circuit" is especially useful in the study of cathodic interference problems. There is a tendency on the part of many people to place the reference electrode anywhere on the ground, interrupt the rectifier and construe any change in potential reading, either an increase or a decrease, as indicating interference. This increase or decrease of potential many times is not an indication of interference at all but simply the effect on the electrode of either anodic or cathodic fields associated with the structure under protection.

Figure 11A shows the physical layout of a structure under cathodic protection. Also shown is another structure without cathodic protection in the same vicinity and designated as the "foreign structure". The foreign structure also will have local anodes and cathodes, with currents Iaf and Icf shown as a broken line.

Figure 11B below shows the "equivalent electrical circuit" of the protected structure and the foreign structure. In addition to the circuit of the protected structure, the foreign structure's local anode potential, current, and resistance, Eaf, Iaf and Raf; and the foreign struc-

ture's local cathode potential, current and resistance, Ecf, Icf and Rcf are shown. Also shown is the resistance of the foreign structure itself, Rsf. When measuring structure-to-earth potentials of the foreign structure, the most valid potential will be measured only when the reference electrode is placed in the remote ground portion of the electrical circuit, which is beyond all the local and impressed current, anode and cathode fields. (This remote position may be especially difficult to locate in large network areas.) If the reference electrode is placed anywhere in the field of the cathodic protection anode resistance Rp, the potential measured will include the voltage drop due to the protection current Ip through the resistance Rp when the rectifier is on. This potential drop is additive but unrelated to the actual potential of the foreign structure. A maximum but equally unrelated potential of the foreign structure will be measured if the electrode lead is connected to the positive terminal of the rectifier.
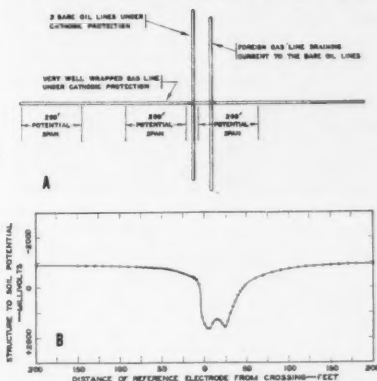
Conversely, if the reference electrode

579t

is placed anywhere in the fields of the cathodic protection cathode resistances Ra or Rc, the potential measured will include the voltage drop due to the protection currents Ipa and Ipc through the resistance Ra and Rc when the rectifier is on. This potential drop is subtractive, but no more related to the actual potential of the foreign structure than those measured in the anodic field. Similarly, the maximum error would be indicated if contact is made to the negative terminal of the rectifier.

Measuring the increase or decrease in current flow on the foreign structure itself by taking the potential drop along a section of the structure's resistance Rsf is usually a more reliable criterion of interference. Any change with the rectifier on and off would be considered as interference current, if the two systems are electrically separated. However, this would be a false conclusion if they were electrically connected by accidental contact or by a bond.

Figure 12A shows a very well wrapped large gas line under cathodic protection crossing three bare oil lines under protection; and a foreign gas line, which was draining protection current to the oil lines. Initial tests on the protected gas line with the reference electrode placed near the crossing, in the strong cathodic field of the bare oil lines, indicated potentials of the gas line to be 1660 millivolts positive to a copper sulfate reference electrode when the oil lines were under cathodic protection. To correct this condition and bring the protected gas line back to its original potential would require that 31 amperes be drained to the bare oil lines. Thirty-one amperes would be almost one-third of the amount of cathodic protection applied to this section of the bare oil lines. This amount of current also seemed like a ridiculous value to correct an interference problem on a relatively short length of well wrapped pipe where a lesser amount of current would normally supply adequate protection for a distance of 25 to 75 miles.

A potential profile was then obtained by moving the reference electrode in both directions away from the crossing, as shown in Figure 12B. These positive potentials were measured for a distance of less than 50 feet in either direction from the point where the major cathodic field was observed to exist.

Potential drops across 200-foot spans were measured at the three locations shown in Figure 12A. No change in span potentials nor the potential to a remote reference electrode was observed at any of the three locations when the rectifiers on the oil lines were interrupted. It was therefore concluded that no interference existed.

This is a typical example of a case where an extreme amount of cathodic interference was indicated by the soil potential method, but no measurable interference actually existed. This example, and other similar ones, where the reference electrode is placed in a strong cathodic field, appears to be a case where the "Criteria for Cathodic Protection," enunciated in the Report of NACE Committee T-2C[3] is not applicable.

Deceptively-simple structure-to-soil po-tential measurements actually can be complex and misleading. A few potential readings taken at random by the novice are of no true significance to him or anyone else, but when these are adequately gathered and properly analyzed, a great amount of useful information about underground structures may be obtained.

The "Equivalent Electrical Circuit Analogy" has proved very helpful and enlightening in analyzing test data. The author's organization is continuing its studies, with the hope of achieving correlation with corrosion coupons and leak data. It is hoped that this description of a useful concept of structure-to-soil potentials will stimulate constructive contributions to the subject.

References

1. National Academy of Sciences and National Bureau of Standards, Federal Construction Council Technical Report No. 32. Cathodic Protection as Applied to Underground Metal Structures.
2. R. H. Brown and G. C. English. Electrochemical Principles of Cathodic Protection, from Cathodic Protection, a Symposium, The Electrochemical Society and National Association of Corrosion Engineers, 1949, p 7.
3. Criteria for Adequate Cathodic Protection of Coated, Buried or Submerged Steel Pipe Lines and Similar Steel Structures. A Report of NACE Technical Unit Committee T-2C on Criteria for Cathodic Protection. *Corrosion*, 14, No. 12, 561t (1958) Dec.

a be
ntial
ovice
any-
ately
great
un-
l.
cuit
and
The
its
orre-
leak
n of
po-
con-

n to
elp-
l in
lar,
H.
roco

Bu-
uncil
ction
s.
emi-
from
ctro-
n of
Lines
of
C on
14,

Service Experience With

Lead-Silver Alloy Anodes
in
Cathodic Protection of Ships*

By K. N. BARNARD, G. L. CHRISTIE and D. G. GAGE

Abstract

An alloy of lead-2% silver has been used experimentally as an impressed current system for cathodic protection of an active destroyer. This paper describes the anodes and their associated equipment and method of fitting. Data are given on the performance of this system after one year's service and comparison of performance and costs are made with existing impressed current and galvanic systems.   5.2.3

Introduction

THE POSSIBLE use of load alloy anodes for the cathodic protection of ships was first suggested by Crennell and Wheeler.[1,2] They had conducted laboratory experiments on pure lead and lead alloys as anodes in sea water and their results indicated that lead alloyed with a small percentage of silver gave coulomb efficiencies equal to or better than the best grades of graphite anodes. This high coulomb efficiency is due to the formation of a protecting film on the lead alloy which slows the attack on the underlying metal. As the peroxide is electrically conducting, its presence does not markedly affect the anode resistance, provided it remains in contact with the metal substrate, i.e., no non-conducting compounds of lead are formed between the peroxide layer and the metal. Crennell and Wheeler had shown that, in sea water, pure lead was not a good anode material, due to the tendency to form the non-conducting compounds beneath the peroxide.

Confirmatory laboratory experiments were made at the Naval Research Establishment with a number of lead alloys, of which the alloys: Lead 98%, silver 2%; and lead 98%, silver 1%, tin 1%, appeared the most satisfactory. One anode of each of these alloys was cast and fitted to an active tug early in 1955. In service, the alloy with the 2 percent silver gave the better performance and showed excellent promise of being a suitable inert anode for the cathodic protection of slow speed ships.

The suitability of the anodes for high speed ships, such as destroyers, was still open to question, because the peroxide layer under these conditions had to withstand the high water speed and vibration associated with such craft. To test the anodes on such ships ten anodes (lead 98%, silver 2%) were fitted to HMCS Crusader, a destroyer, in July 1956.

This report describes the method of installation of the anodes and associated equipment, discusses operational experience, and makes economic comparisons with other anode systems.

Components of the Cathodic Protection System

The cathodic protection system fitted to HMCS Crusader consisted of (1) two sizes of lead—2 percent silver anodes, Mark I for fitting under the ships counter and Mark II for fitting on bilge keels; (2) anode brackets of gum plastic sheeting; (3) current shields of polychloroprene; (4) rectifiers and appropriate wiring and glanding; and (5) hull mounted reference electrodes.

Manufacture and Fitting of Lead —2% Silver Anodes and Brackets

Manufacture: The anodes were cast from lead ingot and silver bar in the proportion 98:2. The resultant alloy after casting analyzed well within the desired range of 2% silver ± 0.1%. (Subsequently, anodes have been cast from alloyed lead—2% silver ingots, obtained from a metal supplier, with negligible change in alloying content on casting.) The anodes were mechanically sound and free from blowholes, sand inclusions and hot tears. An exploded view of a Mark I anode assembly (of which two were fitted) is shown in Figure 1. The Mark II anode (of which eight were fitted) differs from this in overall length of exposed faces and cable connection.

The bracket material was gum plastic sheeting used in two thicknesses: a

KENNETH N. BARNARD—He is a graduate of the University of Saskatchewan with a BSc and an MSc. His work at HMC Dockyard, Halifax, N. S. has been largely on investigating and preventing corrosion of underwater hulls of naval ships.

Barnard

Christie   Gage

G. L. CHRISTIE—Born in Western Canada, he graduated from the University of Saskatchewan with BSCE in 1937, and from McGill University with PhD in 1948. He has been two years with the National Research Council and six with Aluminum Company of Canada. Since obtaining his doctorate he has been on the staff of Naval Research Establishment, Dartmouth, N. S. working on corrosion and metallurgical problems.

D. G. GAGE—Born in the USA, he came to Canada at an early age. After army service in World War II he attended Mount Allison University, graduating with a BSc in 1950. He received his MSc from Dalhousie University in 1953. He has been two years with the Fisheries Research Board of Canada and seven with the Defense Research Board's Naval Research Establishment in the Chemistry Section.
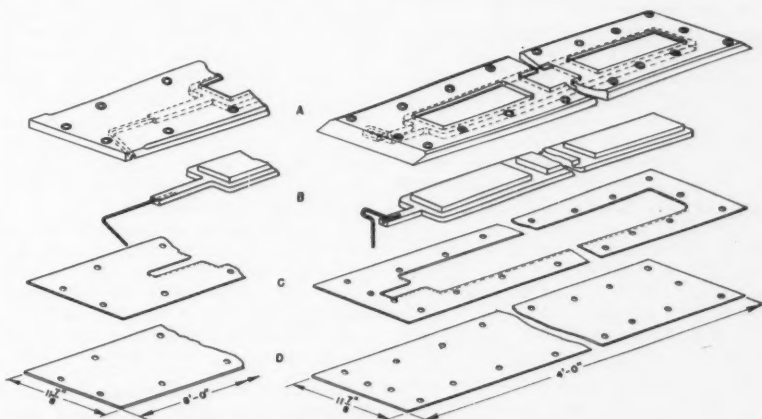
Figure 1—Exploded view of Mark I lead alloy anode. Cable connection for Mark II is seen at left. A. Bracket. B. Anode. C. Polychloroprene gasket. D. Backing piece.

41

1-inch thick sheet, which formed the main bracket or cover, and an 1/8 inch sheet, which served as extra insulation below the anode and was used to hold it in place in the main bracket for ease of handling prior to installation. The cutting and machining of the stock was carried out in such a way as to leave the cover and back in single lengths.

The brackets for the Mark II anodes were made in matching pairs with left and right hand grooves for the anode cable leads. This facilitated the mounting of the anodes in pairs and ensured that both cables would point towards the gland outlet for the pair. A sheet of polychloroprene (1/16 inch thick) was used as a gasket seal between the cover and backing pieces in all cases. The unexposed anode faces were coated with polychloroprene sheeting, 1/32 inch thick, using cold-bond solutions, to prevent corrosion on these faces and loosening of the anode in the bracket.

The conducting cable connection was made by soldering the wire in a slot cut into the lug cast on the end of the anode for this purpose. The joint was then wrapped with tape, the anode placed in the bracket with the cable placed inside the groove especially cut in the bracket. The cable was then covered with polychloroprene putty to ensure a water-tight joint. After these operations the backing plate was fastened to the main bracket with small counter-sunk brass screws.

Fitting of Anodes. Because hull plating at the stern is relatively thin, the Mark I anodes (Figure 2) were fastened to a ¾ inch mild steel (1x4-foot) backing plate welded to the hull. This plate was drilled and tapped to correspond with the anode bracket and gland opening. The Mark II anodes were mounted on the bilge keels in pairs, so that the ends with the cable connections butted together. The exact positions of the anodes were determined by the relative ease with which the gland, cofferdam and standpipe could be positioned inside the hull. The anodes were mounted with one pair towards the fore end and one towards the aft end of the bilge keel. The assemblies were secured in place with counter-sunk cap screws covered with polychloroprene putty.

Current Shields. Before installation of both Mark I and Mark II anodes the polychloroprene current shields were applied. These extended three feet in all directions from the anode. Later inspections showed that this should be increased to four feet. When it was necessary to lap sheets the vertical joint was made so that the forward lapped over the aft sheet in order to avoid possible lifting due to water action at the faying edge. The horizontal joint was made at the junction of the upper bilge keel surface to the hull plating. Previous experience had shown that when anodes are fitted to the topside of bilge keels, it is more important to provide a wider current shield on the hull immediately above the anodes than below. For this reason, the full width of the sheet was

Figure 2—Mark I anode as fitted.

used above the bilge keel, whereas the lower sheet, starting from the hull junction, covered the top surface of the bilge keel and only about half of the bottom surface, from the edge in.

Previous experience with polychloroprene sheeting bonded to steel hulls had shown that it was necessary to prevent water action at high speeds damaging the edges of the sheets, particularly at the leading edges. To accomplish this, steel strips were tack-welded around the edges of all the sheets, as shown in Figure 3. The cross-section of the steel strip was slightly crimped in order to give the edge over the plastic sheet a slight spring action when the strip was welded in place.

Glanding, Cofferdams and Standpipes. Single-holed glands, as shown in Figure 4 were used for the Mark I anode cable and the double-holed glands were used for the Mark II anode cable pairs. A spiggotted backing pad was used with each type of gland. The pads were held in place by continuous welding, both on the inside and outside, to prevent water seepage between pad and plating.

The cofferdams were as large in size as could be conveniently fitted, consistent with the space available and the possibility of making water-tight welds. A removable cover was fitted for access to the gland and anode cable. The waterproof connection between anode and supply cables (a straight splice covered with tape) was made inside the cofferdam. Standpipes were used to carry the cables from the cofferdam to two feet above the waterline.

Electrical Cables, Connections and Rectifiers. The anode lead was a short length of stranded single conductor 7/064 polychloroprene cabtire cable.
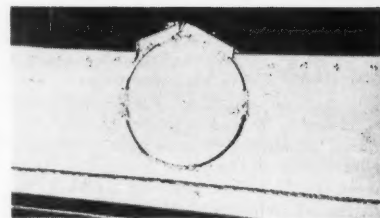

Figure 3—Polychloroprene sheeting as applied, showing securing strapping.

This size of cable was the largest that could conveniently pass through the hull gland and fit a slot in the anode bracket in such a way as to make the water-tight seal previously described. Each anode had its own supply cable to give flexibility and reduce effects of lead breaks or shorts. The lengths of the electrical supply cables between rectifier and individual anodes varied, but the choice of diameter was fixed by the condition that the total resistance of any one cable should be less than 0.2 ohms.

Two rectifiers (each 440 v 3-phase AC to 0-12 V DC, 0-100 amp) were used, one on each side of the ship to serve the anodes on the corresponding sides. Terminal lugs and strips were used so that the individual anodes could be connected or disconnected at will. The rectifiers were mounted in the gearing compartment of the ship and each had its own voltmeter, switches, ammeter and variac transformer for current control.

Reference Electrodes. Two silver-silver chloride reference electrodes were mounted on the hull at positions one quarter of the ship's length from the bow and on the keel just aft of the "A" brackets. The method of mounting these electrodes is shown in Figure 5. A standard
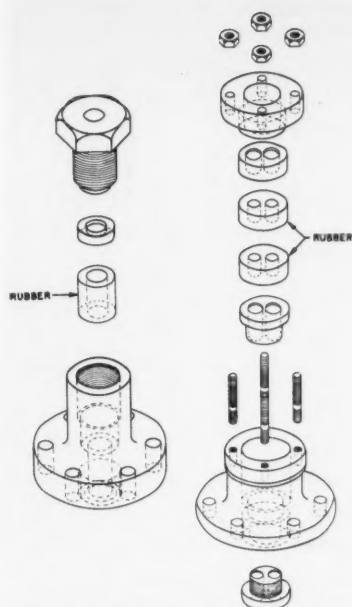
Figure 4—Shipside glands for anode cables.

Figure 5—Hull mounted reference electrode.

ship-side gland, cofferdam and standpipe were used and the electrode leads were brought to the same compartment in which the rectifier units were mounted. In addition to these the hull potential could also be measured with the standard over-the-side electrode and portable millivoltmeter. This meter and the mounted one at the rectifier panel had an internal resistance of 20,000 ohms/ volt.

Operational Procedure

Previous experience with lead-alloy anodes had indicated that the anode current density should exceed a minimum of 3 amp/sq. ft. to form a tight peroxide film that would prevent attack on the underlying metal and resultant shortening of the 10-year life expectancy of the anode. It was also known that the current density requirement of a freshly painted hull is low. For these reasons,
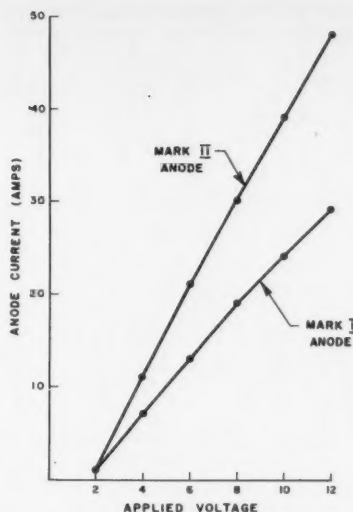
Figure 6—Current-voltage relationship for Mark I and Mark II anodes.

some of the anodes were left unconnected on undocking the ship and a proposed schedule for making the connection was drawn up, so that the anodes in use were always delivering more than 3 amp/sq. ft. Additional considerations in drafting the schedule were (1) maintenance of even current distribution over the hull with variations in current demand, (2) the maintenance of the optimum hull potential, (3) maintenance of the minimum supply voltage that would be compatible with other requirements, and (4) the current-voltage relationship of each anode as found immediately after undocking. Typical values for the latter are given in Figure 6.

Daily readings of the hull potential with both the portable and hull-mounted electrode systems and of the anode current and voltage were scheduled when the ship was in a steady state, either at rest or in motion and the current adjusted to hold the hull potential at the designated value. (820-840 millivolts.)

When, for example, the ship started to move, a current increase was scheduled. The suggested increase was 20 percent until experience with the particular ship dictated otherwise. When a change in current had been made, the hull potentials were to be checked a half hour after such change to determine if the change had the desired effect. Variations in hull current and measurements of potential would then be made at intervals thereafter as required, until the optimum hull potential was reached.

In order to avoid frequent coupling and uncoupling of anodes due to current demand changes with motion, the schedule was made broader than minimum anode current density and power considerations would dictate, i.e., some sacrifice of power was made in the interests of convenience.

The over-the-side reference electrode readings were scheduled as the standard value for the hull potential, until it had been established that the hull-mounted electrodes gave comparable readings.
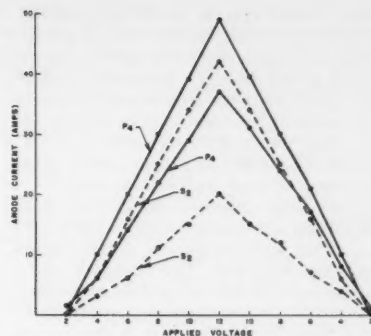

Figure 7—Current-voltage relationship showing recovery when unused anodes are connected to the system.

When this happened, the over-the-side readings could be taken once a week as a check or, if erratic readings were obtained from the hull-mounted electrodes at any time. Daily readings with the hull-mounted electrodes were scheduled, first with the anode current on and then with the anode current off momentarily.

Operational Experience

On undocking in July 1956, the current-voltage relationship for each anode was obtained and the typical results shown in Figure 7 were used for scheduling of the anode connections.

Unfortunately, the available AC supply with the ship berthed was overloaded and it was not possible to provide power to the system from this source. A junction box for shore power was planned for the system, but was not installed until some seven months after the ship had been undocked. When at sea, power was taken from a generator used to run special equipment needed only at sea. Thus, for the first seven months, the anodes were activated only while the ship was underway and the plot of current demand against time during this period is not continuous and the potential time curve shows wide fluctuations. Furthermore, the number of anodes in use was increased above the normal requirement to allow reasonably quick buildup of protection during the time the ship was underway.

It was soon observed that the hull potential as read by the hull-mounted electrodes was within 10 mV of that given by the over-the-side reference electrode. This is believed to be fortuitous for the case of the stern reference electrode as the stern anodes and two large cathodes (the propellers) were close by, and it indicates that by strategic placement of the reference electrode, it is possible to obtain "hull potentials" that are useful in the stern area. It was also noted that the response of the stern electrode to a current change was much quicker than for the forward electrode, a not unexpected effect but one that may prove important in automatic current control. The response of two reference electrodes —one near the field of an anode and one at a distance from it—can give better sensing of the effects of current

changes than can be obtained from distant electrodes because the rate of polarization of large structure is rather slow.

The graph of the current-hull potential relationship is shown in Figure 8. The current demand for protection of this ship was rather less than that required for similar destroyers using magnesium and steel anodes, because there was no large wastage of current near the anode, the plastic current shield had the effect of moving the anode array from the hull and, the energized stern anodes close to the propellers were used.

Because current demand was relatively light most of the time only four, or at the most five, anodes were energized in order to maintain the hull potential and to meet the minimum current density requirement. As a result, some of the anodes were not used before the ship was drydocked in July 1957. Just prior to this drydocking, tests were made to determine whether there had been any change in the current-voltage relationship of the anodes with time; i.e. if the peroxide layer formed during the year changed the initial anode resistance. All anodes used and unused were tested with the results given in Figure 7, 9-10. Here the designations "P" and "S" refer to the side of the ship and the anodes are numbered from fore to aft thus P5 and S5 are the Mark I anodes at the stern.

The ampere-volts readings were taken with the voltage both increasing and decreasing in uniform steps as shown by the graphs.

The anodes in use at the time the readings were taken (June 29, 1957) were P_1, P_3, S_3 and S_5 and the current-voltage relationship was very close to that for the original readings taken shortly after fitting, indicating a negligible resistance change. The five anodes, P_2, P_4, S_1, S_2 and S_4 that had not been used during the year showed distinctly lower amperes per volt. (Figure 10) In order to determine if they would recover from the effect of disuse, two of the anodes, P_4 and S_2 were substituted for P_3 and S_3. Three days later, the current-voltage relationship was again found for these anodes with the results shown in Figure 7.

From this figure, it can be seen that the anodes quickly recovered from the effect of disuse. This was partly indicated by the increase in current output for corresponding voltages in Figure 10 for the unused anodes as the voltage was decreased from the maximum of 12 volts. The change in resistance was probably due to the formation of a corrosion film over the anode surface more resistant than the peroxide film. From Figures 7 and 10, the effect of the longer cable runs to the forward anodes, P_1, P_2, S_1 and S_2 compared to those for P_3, P_4, S_3 and S_4 can be seen in spite of the fact that quite low resistance cables were used as conductors.

Inspection of Ship After One Year

An inspection of the ship, carried out early in July 1957, showed very little evidence of anode consumption on those anodes that had been in use continuously. The anodes that had been in use for the
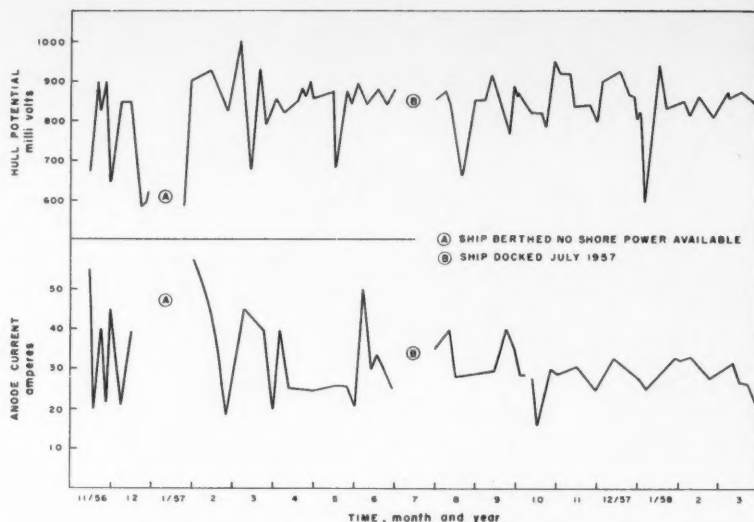

Figure 8—Relationship of anode current and hull potential with time.

(A) SHIP BERTHED NO SHORE POWER AVAILABLE
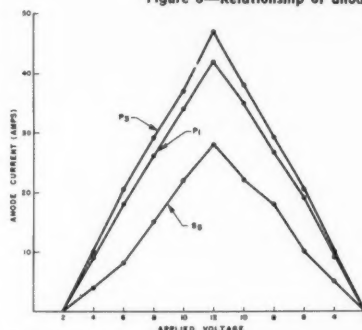(B) SHIP DOCKED JULY 1957

Figure 9—Current-voltage relationship for anodes in continuous use.
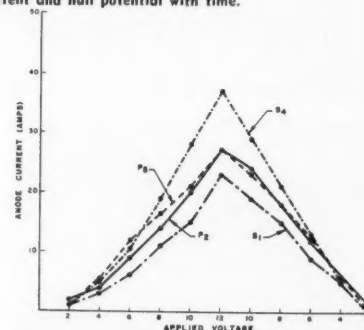

Figure 10—Current-voltage relationship for anodes not in use.
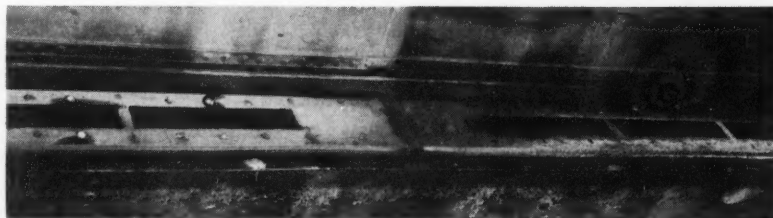

Figure 11—Adjacent anodes in use one year (left) and three days (right). Note paint stripping and wrinkles on insulating sheet and cathodic deposit on securing cap screws.

three days prior to docking (P_4 and S_2) showed very little difference from those in continuous use. For the active anodes, the peroxide film was intact and very thin and the height of the surface of these anodes was approximately the same as that of the unused ones, i.e., the anode surface was still about ⅛ inch above the surface of the bracket material.

In Figure 11, the adjacent parts of an anode used three days and a continuously used anode are shown. From this photograph, it may be seen that, in addition to the small anode loss mentioned above (a) there is cathodic deposit at the heads of many of the retaining screws; (b) the sheeting above the forward anode had come away from the hull as can be seen by the wrinkling; (c) there was no noticeable deterioration of the bracket

material; (d) the steel straps around the edges of the neoprene sheeting had held the edges securely; and (e) the paint was in poor condition.

In regard to (a), the face of the brackets was not covered with sheet during installation as originally intended, and the need for such a covering in addition to the putty is indicated. The loosening of the sheeting (b) is a more serious defect. In applying the polychloroprene, it is part of the technique to remove the air from blisters with a hypodermic needle and roll the sheet flat. This procedure leaves a hole in the sheet, which is partly taken care of by overcoating with cold-bond solution, but the resulting film is susceptible to hydrogen blistering and, in some instances this will lift the sheeting away from the hull. When the

TABLE 1—Principal Characteristics of Alternative Installations

Anode System	Expected Life Time Years	Streamlining	Ruggedness	Maximum Current Density	Ease of Fitting
Lead-2% Silver	10+	Good; (bracket 1" thick). Test indicates overall thickness may be halved.	More than graphite or platinum—less than steel and magnesium. Conforms to unevennesses on ship. Excellent shock resistance.	Depends on power considerations rather than anode. Better than graphite; slightly less than platinum.	Requires current shield and special bracket as do graphite and platinum. Easier to fit and cheaper than graphite bracket. More expensive than platinum bracket. Labour for fitting less than steel, more than magnesium.
Steel	3 (renewable every three years)	Fair, not as good as lead-silver; thicker bracket.	Anode rugged but wooden bracket susceptible to mechanical damage and subsequent loss of sections.	Depends on power considerations and expected lifetime of anodes.	Does not require current shield. Wooden bracket must be facricated to conform to contour of bilge keel. Steel anode sections difficult to handle and to adapt to contour of bilge keel.
Platinum 90-10 (Pt-Ir) alloy 10 mils thick	10+ (indefinite if not damaged and remaining intact).	Good, same as present lead-silver. Bracket of lucite 1" thick.	Thin foil platinum anode susceptible to tearing. Platinum clad on less noble substrate more rugged but still susceptible to pinholes and corrosion attack on substrate.	Limited only by power considerations.	Requires current shield and special bracket. Bracket less expensive than for other impressed current systems. Fitting labour same as for lead-alloy.
Graphite	10 years	Poor. Requires 3" thick, short versalite bracket.	Poor, Graphite fragile, susceptible to cracking and shocks.	Limited to 10 amps per sq. ft. to maintain 10 yrs. life. Less than lead or platinum.	Requires current shield and costly bracket. Difficult to adapt to hull contours. Must be used in short, thick sections only.
Magnesium	2 years	Poor due to irregular corrosion pattern and discontinuous structure of anode array.	Very good. Poor corrosion pattern resulting in necking at securing straps. May cause sectioning and loss of portions of an anode necessitating earlier replacement.	1 amp/ft² may be limited further by circuit resistance.	Easily fitted, no current shield required. Can be adapted to mild changes in hull contour.

TABLE 2—Relative Costs of Anode Installations for Destroyers

Item	Lead Alloy	Magnesium	Steel
Cost of fitting (including overhead)			
Labor	$2800	$1556	$ 8248
Material	1000	980	3192[1]
TOTAL	3800	2536	11440
CAPITAL COST			
Anodes (complete)	$2443[2]	$3000[3]	Included above
Rectifiers and cable	1754	Rectifiers not required	Not required
Plastic shield	900	Not required	
GRAND TOTAL	$8897	$5536	$11440

[1] Material cost includes anodes and rectifiers.
[2] Eight Mark II anodes, Two Mark I anodes.
[3] 30 anodes.

blister becomes large enough, the sheet either breaks or is torn by water action, thereby spoiling the current shield. Ease of application and effects of puncturing with the needle can be both improved by the use of two sheets of 1/32 inch material rather than the single 1/16 inch sheet. (c) The paint, mostly the anti-fouling paint, failed close to the anode shield and at distances away from the anodes.

The failure of the undercoating was slightly worse near the edges of the shield, indicating that the width of the shield above the anode was a bare minimum for this point. It is to be noted with interest that where the A/F paint was applied over the current shield, it was in better condition than on the hull plating, i.e., with an impermeable barrier under the paint alkaline attack was absent even though near the anode.

Discussion

Electrical and Mechanical Considerations

In view of the relatively short experience with the lead-silver alloy anodes no specific coulomb efficiency can be quoted. From the results of the test to date, however, it can be said that provided the minimum anode current density of three amperes per square foot is maintained, the anode will have a life expectancy greater than 10 years.

The properties of this system such as streamlining ruggedness, expected life,

ease of fitting, maximum available current and density are compared in Table 1 with steel, platinum, graphite and magnesium anode systems.

It is seen from the table that lead-2% silver anodes without considering over all economics are comparable in desirable properties to steel and magnesium on the overall picture and rate better than graphite or platinum because of their greater ruggedness.

Economic Considerations

The economic considerations can be broken down into three sub-headings, capital costs of anodes and brackets, cost of fitting and cost of operating. The capital costs and fitting costs for lead alloy, magnesium and steel are given in Table 2.

The primary cost for the platinum alloy is the price of the platinum itself. Because no noticeable loss of the platinum alloy (90% platinum, 10% iridium) has occurred on the anodes in use for over four years, it is assumed that there would be a high salvage value for the platinum and the capital cost in this case would be equivalent to the interest rate on the capital for the platinum.

The prime cost for the graphite anode assembly is its bracket because graphite is cheap. To give the graphite mounted on naval ships good protection against shock a special type of bracket is required. The bracket material used for the

graphite was the same as for the lead-alloy anode brackets. However, for comparable area of anode working face, about three times the amount of bracket material is required for the former, with the result that for equivalent current per volt the graphite anode assembly costs almost twice that of the lead-silver anode assembly.

Because all permanent anode systems require shielding and the shields are distributed over the hull in the same way, cost of fitting will be the same in all cases. Considering this in view of the above remarks on capital costs for lead, platinum and graphite and the fact that for the lead anode the bracket cost is 58 percent of the assembled anode cost, it is concluded that the lead-silver system would have the lowest capital cost. This statement assumes that over a 10-year period interest charges on the capital invested in platinum would exceed the cost of a lead silver anode and its bracket.

Table 2 gives comparative costs for lead, steel and magnesium anodes on destroyers. With a 10-year anode life for lead, and a two and three year life for magnesium and steel respectively it is seen that the lead-silver system is the more economical.

Cost of Operation

For equivalent capital cost of anode and bracket, the ratio of working areas of platinum alloy, graphite and lead alloy anodes would be 1:7.5:15 and hence the power costs per anode would be approximately in the reverse ratio. For a ship with its underwater hull in a given condition the minimum current demand for protection is more or less fixed, so that the power demand can be minimized only by using the least voltage required to produce the current. This again, is dependent on the geometry of the anode.

At the same equivalent cost per working anode, lead-2% silver alloy would show lower operating cost. However on the overall picture such a comparison cannot be used. For permanent anodes with plastic shields, power costs of a sys-

tem in being would be the same for lead, graphite and platinum. Because of the better current distribution resulting from the use of shielding, the current required for protection with the lead-silver system described is less than that required for presently used steel systems.

However, because the steel anodes require less driving voltage these higher currents put out by steel systems result in the same power output. Thus actual power cost would be approximately the same for all the impressed current systems being compared and only a galvanic system such as magnesium would offer any substantial saving. It can be concluded from the properties tabulated in Table 1 and the economic analysis made above that lead-silver anodes compete very favorably with other presently used systems.

It should be stressed here that the order for the capital costs is based on a predicted performance for the lead-alloy anode and the estimated costs of production of the anodes using the facilities available to date. If production was undertaken commercially, there is no doubt that costs would be radically altered, but it is still believed that they would favor the lead-alloy system, particularly if further experience indicates that a life longer than 10 years can be expected, or that the thickness of the anode can be halved and still give a minimum 10-year life.

From the foregoing discussion it is seen that lead alloy anodes offer many advantages over competing platinum and graphite systems as a permanent inert anode and also a number of advantages

over steel and magnesium anodes.

General Observations

In common with all permanent anode systems, a good, high-duty current shield must be used around the anode. To date, polychloroprene sheeting has proved to be the best available material for the shield, but a better material or improved ways of bonding it to the hull plating should be sought. It has been suggested that two thin sheets of material be used rather than a single thicker sheet. Cheaper substitutes also should be sought for this sheeting, because it constitutes a fairly large fraction of the fitting cost of permanent anode systems.

For permanent anode systems, those that require the least applied voltage are to be desired from point of view of shielding, because there would be less voltage applied across the shield material immediately adjacent to the anode. This means, in essence, that the permanent anode with the largest working face is to be preferred. The 4 x 60-inch working face of the Mark II is thought to be close to the practical maximum length for handling on a bilge keel. Such an anode weighs about 150 lb and until installed, reasonable care must be taken to prevent excessive flexure. As stated earlier, the 4 x 36-inch Mark I anode face is considered the practical maximum for mounting at the stern.

The use of energized stern anodes is evidently very worthwhile, because in this location they apparently reduce the total current requirement for protection.

Major disadvantage of the lead-alloy anode compared to platinum or graphite anodes is the dependence on the peroxide

film to protect the underlying metal against corrosion and the maintenance of a minimum anode current density to form this film. However, provided this minimum anode current density is maintained, it would appear that the protective film is adequate even at high ship speeds and a long anode life can be expected. Moreover, if the film suffers damage, it is self-healing—a distinct advantage when compared with platinum clad anode.

The use of hull-mounted electrodes is more convenient for the measuring of hull potentials than the over-the-side electrodes. Because there appears to be very little difference between the readings obtained with either type when the former electrodes were out of the immediate field of the anodes, the use of over-the-side electrodes need only be resorted to for checking the hull-mounted electrodes.

Acknowledgment

References

1. J. T. Crennell and W. C. G. Wheeler. Private communication.
2. W. C. G. Wheeler. Lead As A "Permanent" Anode for Cathodic Protection. ACD Report M/12/55, Admiralty Chemical Department, H. M. Dockyard, Portsmouth.
3. K. N. Barnard. *Chem. and Ind.*, 1954, pp 172-182.

Electrical Bonding of Cathodically Protected to Unprotected Ships*

By Cdr. G. A. BENNETT, R.A.N.,[1] N. S. DEMPSTER,[2]

and A. J. WALLACE[3]

Abstract

This study has established the need for low resistance electrical bonding between a cathodically protected and an unprotected ship when berthed together. On the basis of three series of electrical measurements, a maximum bonding resistance of 0.0005-ohm is recommended. Calculations based on these measurements show that an instance of severe underwater hull corrosion was attributable to inadequate bonding of an unprotected ship to a cathodically protected ship berthed alongside.   5.2.5

Introduction

THIS investigation arose from the observation of severe underwater hull corrosion of the destroyer H.M.A.S. Warramunga prior to the fitting of a cathodic protection system to it. On several occasions H.M.A.S. Warramunga had berthed alongside the cathodically protected destroyer H.M.A.S. Arunta. The possibility that corrosion was attributable to the adjacent berthing of a cathodically protected ship had been considered, no data were available on the extent to which the steel ropes used to secure the ships would serve as an electrical bond.

The Cathodic Protection Sub-Committee of the Naval Corrosion Committee (Royal Australian Navy) undertook this investigation primarily to establish the degree of electrical bonding required to reduce the extent of such corrosion to negligible proportions and incidentally to determine whether the previously reported incidence of corrosion could have been attributable to ineffective electrical bonding of the two ships concerned.

Ships employed in this investigation were:

1. The Tribal class destroyer H.M.A.S. Warramunga which, by the time of this investigation, had been fitted with an impressed current cathodic protection system using mild steel anodes mounted on the bilge keels and a further 35-foot steel anode mounted on the keel line in the "cut up" aft.

2. The Battle class destroyer H.M.A.S. Tobruk, which was not fitted with cathodic protection.

H.M.A.S. Warramunga had been painted according to the following schedule: 1 coat vinyl wash primer (specification MIL-P-15328); 3 coats zinc chromate pigmented vinyl anti-corrosive (specification MIL-P-15930); 2 coats vinyl antifouling (specification MIL-P-15931).

H.M.A.S. Tobruk had been painted to the following schedule: Red oxide-zinc chromate primer; Oleo-resinous anticorrosive paint; A conventional mercurial antifouling paint.

Methods of Measurement

It was recognized that a portion of the current leaving the anodes of a protected ship could flow to a neighboring ship and return to the former ship's hull via a low resistance sea-water path in parallel with some form of bonding such as the steel ropes. This provided the basis for the following three methods devised for determining the effectiveness of various electrical bonds:

(a) The IR drop method

(b) Measurement of potential between the two hulls.

(c) Measurement of anode-to-hull potentials.

Methods (a) and (b) were initially devised and were considered capable of providing adequate indication of the effectiveness of various electrical bonds. In the course of the investigation it was realized that method (c) would not only achieve this purpose, but would also furnish the approximate resistance of the various current paths and thereby means of calculation of the current flow.

(a) The IR Drop Method

The schematic diagrams of Figure 1 show the direction of current flow from one anode of ship W and the possibility of current entering ship T by the sea-water path r_1, and returning by either the sea-water path r_x, the steel ropes r_s or the electrical bond r_b. The IR drop involved in the return current path is obtained by measuring the change in potential between ships W and T with the protective current on, and immediately after switching the current off. The extent to which the electrical bonding is effective is therefore indicated by the order of the measured IR drop.

(b) Measurement of Potential Between the Two Hulls

From Figure 1 it is apparent that as the bond resistance r_b is diminished, the potential measured between ships W and T will also diminish until, at some infinitely small value of r_b, the potential between ships W and T will approach zero. At this stage practically all of the current returning to the hull W will be flowing through the bond. Therefore with the cathodic protection system operating on ship W, the order of potential measured between ships W and T will give

an indication of the amount of current returning via the external electrical bond.

(c) Measurement of Anode-to-Hull Potentials

This method was adopted in an attempt to determine the current flow through the various conducting paths such as the bond, the steel ropes and the sea-water paths by determining their respective resistances.

For the three conditions represented by Figures 3, 5 and 7, measurement was made of:

(1) Potential between the anode of ship W and the hull of ship T.

(2) Potential between the anode of ship W and the hull of ship W.

(3) Total anode current.

If the resistance of the electrical bond r_b is known, it is then possible to derive the resistance of the various conducting paths and from these values to determine the current flow in these paths.

Instrumentation

Two types of instruments were used for potential measurements. For the measurements involved in methods (a) and (b) above, a 0-1 volt voltmeter (20,000 ohm/volt) graduated in 10 millivolt divisions was used. For method (c), the 0-1 volt voltmeter was used for measuring the higher potentials but the lower values required a higher degree of accuracy and use was made of a Cambridge type workshop potentiometer covering a range of 0-20 millivolts, which can be extended by the use of a X5 multiplier.
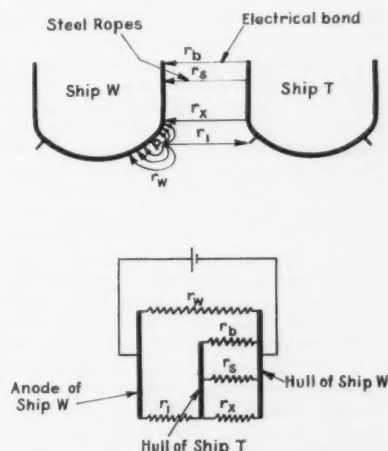

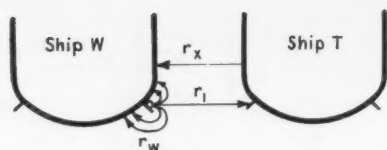Figure 1—Schematic diagram of current paths when ships W and T berthed together and equivalent electrical circuit.

Figure 2—Schematic diagram of current paths when ships W and T berthed together. Steel ropes insulated and no bond. Return current from ship T through sea-water only.
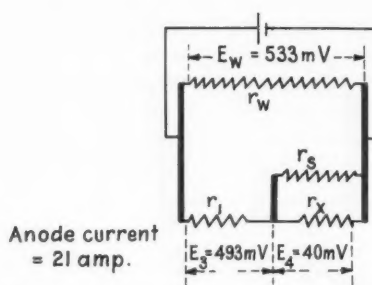

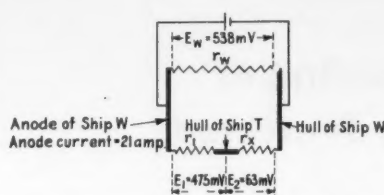Figure 3—Electrical circuit representation of Figure 2.
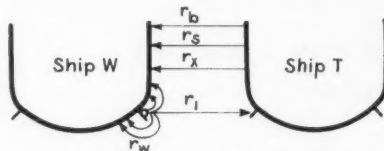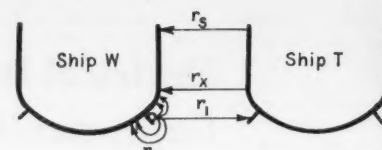

Figure 4—Schematic diagram of current paths when ships W and T berthed together. Steel ropes provide additional current return paths.

Anode current = 21 amp.

Figure 5—Electrical circuit representation of Figure 4.

Figure 6—Schematic diagram of current paths when ships W and T berthed together. Steel ropes and bond provide additional current return paths.

Figure 7—Electrical circuit representation of Figure 6.

Hull potentials were measured against a standard silver/silver chloride reference electrode and all values of hull potential are negative with respect to this electrode.

Experimental Conditions

(a) *The IR Drop Method*

The IR drop was measured under the following four conditions:

1. H.M.A.S. Warramunga, at an average potential of —840 millivolts was brought alongside and secured by manila ropes to H.M.A.S. Tobruk, which was at a potential of —630 millivolts. There was no form of electrical bonding between the two ships; the estimated distance between them was 7 feet.

2. Suitably located eye bolts on the decks in the midships area of the two ships were cleaned of paint with a file and about 10 feet of 50-ampere cable was secured to the eye bolts by ½ inch bolts. (This method is commonly used for earthing leads during DC welding on ships.) Manila ropes were still used for securing the two ships.

3. A lower contact resistance was provided between the bonding cable and the hull, two ¾ inch diameter brass studs being brazed on to the deck plates in adjacent positions midships on both Warramunga and Tobruk. A 12-foot length of 200-ampere cable, fitted with 300 ampere lugs, was used in series with a 0.001-ohm resistance to bond the two ships.

The manila ropes were replaced by steel ropes after it had been shown that the latter made no difference to the values for condition (2).

4. Two 200-ampere cable bonds as described above were fitted in parallel between the ships without a series resistance in circuit. The electrical resistance of this assembly was of the order of 0.0004-ohm. The steel ropes were still retained for securing the ships.

(b) *Measurement of Potential Between the Two Hulls*

The conditions were identical with those in (a) 1-4 above.

(c) *Measurement of Anode-to-Hull Potentials*

H.M.A.S. Warramunga was berthed alongside H.M.A.S. Tobruk so that Warramunga's starboard side was adjacent to Tobruk's port side. The sea-water was of usual salinity and contained 3.2 percent chloride expressed as sodium chloride. In order to simplify measurements, Warramunga's aft and port side anodes were disconnected from the DC supply and the current to the starboard anode was raised to approximately 20 amperes. (This would be approximately three times the normal current from this anode under stationary conditions.) Potential measurements were then made between the inboard lead to the starboard anode and Warramunga's hull and between the anode lead and Tobruk's hull. The difference between these two measurements was checked by measuring the difference in potential directly between Warramunga's and Tobruk's hulls in the midship's area. Using a 0.001-ohm series resistance, measurements were made of the anode current, and, where possible, the current through the bond.

For ease of reference, details of the conditions of measurement are presented in the Results section.

Results

(a) *The IR Drop Method*

The IR drop values obtained for the four bonding conditions outlined in Experimental Conditions (a) 1-4 are shown in Table 1.
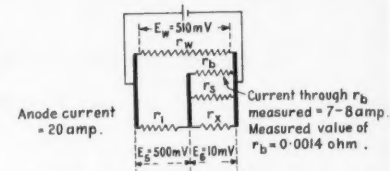
(b) *Measurement of Potential Between the Two Hulls*

In the course of these measurements there was a decrease in hull potential of Warramunga due to the progressive decrease in bonding resistance. Hence, the potential differences shown for conditions 1, 2, 3 and 4 below cannot be strictly inter-compared but are nevertheless indicative of the improvement in bonding.

Condition 1. Potential difference (pd) between the ships was 209 millivolts.

Condition 2. The pd between the two ships was 138 millivolts. The replacement of manila ropes by steel ropes had no immediate effect but after one hour the pd had fallen to 98 millivolts. On disconnection of the welding type bonding cable, the pd rose to 140 millivolts.

Condition 3. With one 200-ampere cable as bond plus a 0.001-ohm resistance in series, the pd was 35 millivolts. With one 200-ampere cable as bond and no series resistance, the pd was 4 millivolts.

Condition 4. With two 200-ampere cables as bond, plus a 0.001-ohm resistance in series, the pd was 30 millivolts.

With two 200-ampere cables as bond and no series resistance, the pd was approximately one millivolt.

(c) *Measurement of Anode-to-Hull Potentials*

Three sets of measurements were made for the conditions existing in the three cases represented by Figures 2, 4 and 6. Figures 3, 5 and 7 depict the same three conditions as electrical circuits and show the values of potential and current measured.

TABLE 1—IR Drop Values for Variously Bonded Conditions

Experimental Condition	Potential Between Warramunga and Tobruk (mv)		IR Drop (mv)	Port, Starboard and Aft Anode Currents Respectively (amp)
	Cathodic Protection On	Cathodic Protection Off		
1 (no bond)	209	191	18	6, 7, 10
2 (poor bond)	135	122	13	6, 7, 10
3 (one cable bond)	35	30	5	6, 7, 10
4 (two cable bond)	3	1	2	7, 8, 11

TABLE 2—Calculated Current Through Various Return Paths for Different Bonded Conditions (See Figure 1)

Case	Current Through Sea-Water Path r_1 (amp)	Current Return Through Sea-Water Path r_x		Current Return Through Steel Ropes r_s		Current Return Through Bond r_b	
		amp	Expressed As % of Current Through r_1	amp	Expressed As % of Current Through r_1	amp	Expressed As % of Current Through r_1
1. Only steel ropes provide bond.................	9.3	5.7	61	3.6	39	..	..
2. Steel ropes plus 0.0014-ohm bond.............	9.4	1.4	15	0.9	10	7.1	75
3. Steel ropes plus 0.0004-ohm bond.............	..	..	5	..	3	..	92

In the first series of measurements, represented by Figures 2 and 3, the steel ropes were insulated from Tobruk's hull by inserting neoprene sheets between the ropes and the bollards and between the ropes and the deck plates. No electrical bond was fitted in this instance, so that the two ships were insulated.

In the second series, represented by Figures 4 and 5, the steel ropes were not insulated on Tobruk but no other electrical bond was fitted.

In the third series, represented by Figures 6 and 7, the steel ropes were not insulated on Tobruk and an electrical bond of 0.0014-ohm was fitted between the two ships.

From the three series of measurements the following three relationships can be obtained:

$$\frac{E_1}{E_2} = \frac{r_1}{r_x} \tag{1}$$

$$\frac{E_3}{E_4} = \frac{r_1}{r_x} + \frac{r_1}{r_s} \tag{2}$$

$$\frac{E_5}{E_6} = \frac{r_1}{r_x} + \frac{r_1}{r_s} + \frac{r_1}{r_b} \tag{3}$$

If it is assumed that these resistances remain constant during the three series of measurements, (1)-(3) can be treated as simultaneous equations and values for r_1, r_x and r_s may be derived and hence values for r_w can also be determined.

The derived values for r_1, r_x and r_s are as follows:

$$r_1 \simeq 0.053\text{-ohm}$$
$$r_x = 0.007\text{-ohm}$$
$$r_s = 0.011\text{-ohm}$$

Values for r_w can be derived from any of the Figures 3, 5 or 7.

Using Figure 3 as an example:

The current through $r_1 = \dfrac{0.475}{0.053}$

$\simeq 9$ amperes.

∴ the current through $r_w \simeq 12$ amperes, since the total anode current was 21 amperes.

∴ $r_w \simeq 0.045$ ohm.

The value of r_w derived from Figure 5 = 0.046 ohm and from Figure 7 = 0.048 ohm.

In practice these resistances may not remain constant due to the following:

(1) The sea-water path resistances include the resistive component of polarization which would vary from one series

of measurements to another according to the change of current density on the hulls brought about by variation of bonding resistance.

(2) The changes of the steel rope-to-bollard contact resistance due to the effect of wind, waves and tides cause some variation of the steel rope resistance r_s. Within any one series of measurements this effect could be minimized by simultaneous recording of potential and current measurements, but this would entail considerable instrumentation, which was not considered justifiable. Furthermore the variation of the r_s value between each series of measurements cannot be controlled.

Nevertheless, it is clear that the anode-to-hull potential measurements have provided a useful approximation to the resistance values of the various conducting paths.

Discussion

Both the IR drop method and the measurement of the potential between the two hulls have provided a measure of the effectiveness of various electrical bonds.

It was noted incidentally in Experimental Condition (3) of the IR drop method that the current through the bond was 15.5 amperes when the cathodic protection system was operating and 12.2 amperes when the cathodic protection system was off. This latter high current was short-lived, of course, but was due to the large cathodic area of the underwater surfaces, as the potential difference between the two ships was only 30 millivolts. It is pointed out that the current flow in the bond circuit without applied current does not invalidate the method, because in these measurements the concern is only with determination of IR drop which is attributable to the flow of current from the anode of the protected ship.

The anode-to-hull potential measurements have provided approximate values for the resistances of the various conducting paths. Using these values, the efficiency of various bonds can be shown by calculating the current flow in the resistances r_x, r_b and r_s. These calculations have been made for the following three cases:

Case 1. Warramunga and Tobruk berthed together with only the steel ropes providing a bond (Figures 4 and 5).

Case 2. Warramunga and Tobruk berthed together with bonding provided

by the 0.0014-ohm bond plus the steel ropes (Figures 6 and 7).

Case 3. The hypothetical case in which the 0.0004-ohm bond was used without the 0.001-ohm series resistance. Here the percentage current return through the sea-water, steel ropes and bond has been calculated using the relationship for parallel resistances

$$\frac{1}{R} = \frac{1}{r_s} + \frac{1}{r_x} + \frac{1}{r_b}.$$

Results of these calculations are shown in Table 2.

Calculated current through the bond for Case 2 is shown in Table 2 as 7.1 amperes. This value agrees well with the measured value of 7-8 amperes (refer Figure 7). While further confirmation may be needed, this result does support the assumption used in the anode-to-hull potential method, namely, that the various resistances remain constant.

The anode-to-hull potential measurements have not only provided a more quantitative appreciation of the need for low resistance bonding but have permitted calculation of the current flow in the various conducting paths for different values of bonding resistance. An upper limit of approximately 0.005-ohm resistance in the bonding circuit is justified on the basis of the above calculations.

This is, of course, in direct contrast to the conclusion of Barnard,[1] who recommended the complete insulation of co-berthed ships. It is clear, however, that Barnard was concerned only with the maintenance of the potential of the cathodically protected ship at a desired value.

Calculation Of Extent Of Corrosion Attributable To Ineffective Bonding

Using the resistance values for the various conducting paths as derived from the measurement of the Warramunga-Tobruk berthing, it is of interest to determine the order of corrosion, in terms of weight loss, which could have occurred in the instance in which the unprotected Warramunga was berthed alongside the cathodically protected Arunta.

Records have shown that for the 12 months prior to the April, 1956 docking of Warramunga, Arunta had tied up alongside for some 63½ days, in which time the total current output from the two anodes amounted to 6270 ampere-days. (The high order of current output was due primarily to the use of a conventional non-vinyl paint system on Arunta.)

Because of the unknown resistance value of the sea-water path from the off-side anode to the unprotected ship, consider only the current output from the near-side anode which amounts to 3135 ampere-days.

From the measurements given in Section (c), (refer Figures 4 and 5) in which two ships were berthed together with bonding provided only by the steel ropes, it can be shown that $\dfrac{5.7}{21} \times 100$, i.e.

27 percent of the near-side anode current will return to the protected ship via the sea-water path, thereby causing corrosion of the unprotected vessel. Assuming that the conditions existing in the present investigation were similar to those in the Arunta-Warramunga berthings, the loss of metal from Warramunga caused by the return current through the sea-water would be equivalent to

$$\frac{3135 \times 27}{100} = 846 \text{ ampere-days.}$$

This would amount to a loss of 47 lbs. of steel. Calculations have shown that this order of metal loss is consistent with the amount of corrosion observed at the April 1956 docking of Warramunga. Alternatively, in terms of cylindrical pits $\frac{1}{2}$ inch diameter and $\frac{1}{8}$ inch deep, it is equivalent to some 6700 pits.

While it is realized that certain conditions in the Arunta-Warramunga berthings could not be duplicated in the present investigation (and in fact the anode current density and the apparent hull current density were known to be different), the above calculations have been made to show the order of the metal loss involved. Because the calculation has been based on consideration solely of the current output from the near-side anode, the derived figure is unlikely to be excessive and conceivably could be up to twice the calculated value.

Conclusions

1. Serious corrosion of the hull of an unprotected ship which is berthed alongside a cathodically protected vessel can be avoided by electrically bonding the hulls so that the hull-to-hull resistance is not greater than 0.0005-ohm. This can be achieved by using two minimum length 200-ampere cables in parallel, firmly secured to $\frac{3}{4}$ inch diameter brass studs brazed to the deck plates.

2. The hull-to-hull resistances of (a) steel berthing ropes and (b) the bonds normally used in DC welding, are well in excess of the above limit.

3. There is sufficient evidence to suggest that the reported corrosion of the hull of H.M.A.S. Warramunga was attributable to the frequent adjacent berthings of the cathodically protected H.M.A.S. Arunta.

Reference

1. K. N. Barnard. *Canadian J. of Res.*, F, 28, 417-437 (1950).

Studies on the Susceptibility of Cathodically Protected Steel to Hydrogen Embrittlement*

By W. H. BRUCKNER[1] and K. M. MYLES[2]

Abstract

Cathodically protected sections of hot-rolled 2-inch steel pipe were subjected to low temperature bend tests. The steels tested were API grades A, B and M (N-80). The presence of a reducible Fe O portion of the mill scale delayed hydrogen absorption. Embrittlement of Grades A and B occurred due to notch formation when adherence of Fe O to base metal was destroyed during cathodic protection. Under conditions of low pH with and without sulfide ion, cathodic protection induced hydrogen absorption, and with sulfide ions present embrittlement of steels A and B was severe. Steel M (normalized) was found to be insensitive to embrittlement during cathodic protection. For the M steel cathodic protection for ten months under conditions of high tensile stress and excessive protection gave no indication of static failure or loss of strength and ductility in destructive tests upon removal from cathodic protection.

5.2.1

1. Introduction

STRUCTURAL steels have for many years enjoyed a reputation for stability and stamina which made possible the variety of large engineering structures representative of modern civilization. Because steels could be controlled in composition and processing to give predictable strength properties and above all, good ductility it was possible to design these engineering structures for maximum safety. The ductility of the steel was actually the "built in" safety factor because localized over-stress in service could be relied on to cause local deformation and so shift the load to larger areas.

The advent of numerous, sudden, brittle fractures in engineering structures ranging from ships and bridges to tanks and pipe lines has shaken the structural engineers' confidence in his ability to economically design safe steel structures for service below 100 F. At sufficiently low temperatures brittle fractures have been known to propagate at an average stress of between $\frac{1}{3}$ to $\frac{1}{2}$ the yield strength. In order to avoid brittle failure it is possible for the designer to specify the use of stainless steels and non ferrous metals such as brass, certain aluminum alloys and magnesium based alloys. However, due to cost, corrosion or other considerations such a solution to the problem often is not attractive.

At an early stage in the experience with brittle fractures it was thought that increasing the cross sectional area of a part of the steel structure could avoid brittle fracture. But when brittle failure occurred even sooner with the "beefed up" section it was realized that the state of stress to which the steel is subjected had an overriding importance over any metallurgical considerations or stress levels involved. Again during the early search for an answer to the brittle fracture problem the effectiveness of hydrogen in contributing to brittleness was given an all pervading significance. It has been amply demonstrated by experiment and in service that given a sufficient hydrogen content normally ductile steel can become a glass-like, brittle material. However, the same characteristics

can be attained under other conditions with hydrogen entirely absent.

It is now recognized that steel may be embrittled by hydrogen but its absence does not assure ductile behavior.

The research which is reported here was initiated in order to determine whether steel structures buried in soil and placed under cathodic protection could be embrittled by hydrogen as a consequence of such cathodic protection. For a coated steel structure underground the current density at the cathode depends upon the area of metal exposed to the electrolyte through holidays. Excessively high current density and high hydrogen discharge levels could exist at such holidays. The conditions for embrittlement by absorption of this hydrogen were to be explored.

2. Materials

The steels used as cathode material were obtained in the form of hot rolled pipe nominally of 2⅜ inch OD. Three steel compositions were tested as representative of American Petroleum Institute grades A, B and M(N-80) whose chemical analyses are given in Table 1 together with corresponding physical properties.

3. Procedure

It appeared desirable to apply cathodic protection to the as-received pipe and to determine the changes in embrittlement and hydrogen uptake resulting from various conditions of cathodic protection. The cathodic protection was accordingly varied to include the following:
a) Constant potential of —0.85 volt to copper half cell in soil-water at pH of 7-8.
b) Constant current of 1 ma/sq. ft. in soil water at pH 7-8.
c) Constant potential of —1.32 volt to copper half cell in soil-water at pH of 7-8.
d) Constant potential of —0.85 volt of copper half cell in soil-water with pH of 2.5 to 3.5.
e) Constant potential of —0.85 volt to copper half cell in soil-water with pH of 2.5 to 3.5 and addition of 5 grms Fe S/liter of electrolyte.

All of the above test conditions were applied to as-received pipe with the hot-

Bruckner   **Myles**

W. H. BRUCKNER is professor of metallurgical engineering and technical director of the Cathodic Protection Laboratory at the University of Illinois. He has written papers on cathodic protection of lead cable sheath and has been active in research on metallurgy and welding problems.

K. M. MYLES is a metallurgical engineer of Argonne National Laboratory, Lemont, Ill., where he is engaged in research on fundamental mechanism of radiation damage to metals. He has a BS and MS from the University of Illinois.

rolling mill scale left on. Additional tests also were made with Grade A steel to determine the effect of removing the mill scale prior to cathodic protection. All tests were made with the cathode embedded in soil which was saturated with demineralized water.

The 2.5 pH for (d) and (e) was established by adding to the soil a solution of HCl in demineralized water in appropriate proportions, according to prior test, to bring about soil saturation and 2.5 pH. During the cathodic protection tests the pH rose to a maximum of 3.5.

Glass jars nine inches ID x 12 inches were used for cathodic protection cells. The cathode under study was placed in the center of the cell and ⅛ inch thick graphite plates were placed as anodes concentric with the cathode at the inner surface of the 9-inch diameter jar. Soil was then placed in the space between and saturated with the desired electrolyte.

The cathode used was not a continuous length of pipe because this would have presented a number of problems in sampling the cathode for hydrogen content and for evidence of embrittlement. The actual cathode used was made up
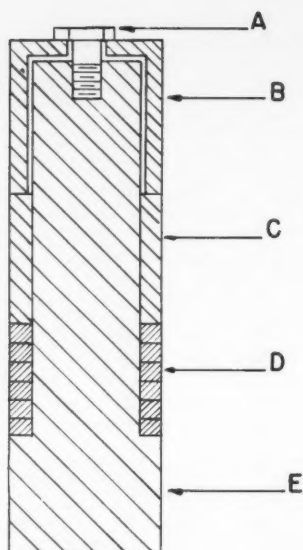
Figure 1—Schematic of assembly cathode. A. Bolt. B. Pressure cap. C. Section of 2½ inch OD pipe. D. ½ inch thick pipe sections. E. Steel mandrel.

of six ring sections, ½ inch wide cut from the as-received pipe. The ring sections were surface ground on the cut surfaces and were assembled on a steel mandrel as shown in the sketch of Figure 1. By means of a bolt and cup arrangement the rings assembled on the mandrel were put into axial compression, thus closing the gap between the cut and ground surfaces and providing essentially a continuous cathode.

The reason for choosing the asembly of ½ inch pipe sections for the cathode was that upon termination of a desired period of cathodic protection the sections could be tested immediately after removing the cathode from the cell. The sections were placed in an acetone-dry ice bath at —100 C and stored with assurance of minimum loss of hydrogen until laboratory operations could be put underway for individual tests of the rings. One of the rings was cut to provide a 5 to 7-gram sample for hydrogen content. The sample along with others was packed in dry ice and shipped by air express to the National Research Corporation for hydrogen analysis by means of the vacuum-fusion methods.

All bend tests were made at —50 C in order to retain hydrogen taken up during cathodic protection and to provide a high level of embrittlement due to any hydrogen content. The bend test results were compared with calibration test data for bend tests made at —50 C on pipe sections of as-received material prepared in the same manner except that they re-

ceived no cathodic protection. Initial hydrogen contents were also determined for the as-received material to serve as a base line in determining the uptake of hydrogen resulting from cathodic protection.

The bend tests were made by placing the ring vertically in a jig contained in a metal box. The box was filled with acetone and dry ice at a temperature of —55 C or 5 C below the desired testing temperatures of —50 C. Upon warming up to —50 C a slowly applied load at a predetermined rate of loading was used to provide plastic deformation in bending across the horizontal diameter. The load was applied by means of a hand operated hydraulic press. The maximum load applied and the rate of loading was determined from calibration tests previously made on the as-received pipe material.

These maximum loads were respectively 5000, 2000 and 3000 lb for steel rings of Grades A, B and M and the bend ductility in calibration tests decreased in this same order. For Grade B and M steels the maximum load of 2000 and 3000 lb respectively represented a load within about 90 percent of causing fracture in bending. For Grade A steel the 5000 lb maximum load represented about a 150-degree bend angle

TABLE 1—Chemical and Physical Analysis of Steel Pipe

Grade	C	Mn	P	S	Yield Point PSI	Tensile Strength PSI	Elongation Percent In 2 In.	Test Pressure Pounds	Wall Thickness Inches
A.........	.17	.40	.009	.033	38000	60300	57	1200	.154
B.........	.24	.53	.009	.032	46800	70600	55	1300	.154
M(N-80).....	.43	1.33	.009 .17 Mo	.020	89300	115900	38	3000	.190

TABLE 2—Results of Tests Made on Steel Rings

Steel Grade	Percent Hydrogen Content	Bend Test
Section 1—Steel pipe as received, not cathodically protected. Mill scale left on.		
A........	0.00018	Few superficial cracks
B........	0.00012	Few superficial cracks
M.......	0.00005	Superficial cracks
Section 2—Cathodic protection for 4 months at constant potential of —0.85 volt to Cu/CuSO₄ and soil-water pH of 7.2 to 8.4. Mill scale left on.		
A........	0.00016 (less than initial)	Superficial cracks
B........	0.00007 (less than initial)	Mill scale: superficial cracks
M.......	0.00003 (less than initial)	No cracks
Section 3—Cathodic protection for 4 months at constant current of 1 ma/ft² and soil water pH of 7.2 to 8.4. Mill scale left on.		
A........	0.00010 (less than initial)	Superficial
B........	0.00006 (less than initial)	Superficial
M.......	0.00008 (larger than initial)	No cracks
Section 4—Cathodic protection for 4 months with excessive overprotection at —1.32 volt to Cu/CuSO₄ and soil-water pH of 7.2 and 8.4. Mill scale left on.		
A........	0.00009 (less than initial)	Moderately severe cracks
B........	0.00005 (less than initial)	Moderately severe cracks
M.......	0.00005 (same as initial)	Superficial cracks
Section 5—Cathodic protection for 4 to 4½ months at constant potential of —0.85 volts to Cu/CuSO₄ and soil water pH of 2.5 initially. Mill scale left on.		
A........	0.00007 (less than initial)	Superficial to severe cracks
B........	0.00028 (slightly more than initial)	Superficial to none

Steel Grade	Percent Hydrogen Content	Bend Test
M.......	0.00058 (ten times more than initial)	No cracks
Section 6—Cathodic protection for 2 months at constant potential of —0.85 volt to Cu/CuSO₄ and soil-water pH of 2.5 initially with 5 grams per liter of FeS added. Mill scale left on.		
A........	0.00055 (four times initial)	Complete fracture
B........	0.00014 (slightly more than initial)	Slight to severe cracks
M.......	0.00013 (four times initial)	No cracks
Section 7—Cathodic protection for 5 months at constant potential of —0.85 volt to Cu/CuSO₄ and soil-water pH of 7.2 to 8.4. Mill scale removed.		
A........	0.00020 (slightly more than initial)	Severe cracks
Section 8—Cathodic protection for 5 months at constant potential of —0.85 volt to Cu/CuSO₄ and soil-water pH of 2.5 initially. Mill scale removed.		
A........	0.00070 (more than initial)	Severe cracks
Section 9—Pickling tests—not cathodically protected, 30 percent by volume mixture of HCl and water to which metallic arsenic had been previously added. Mill scale removed.		
A........	**Immersion Time** 24 hr.	Complete fracture
	2 hr.	Severe cracks
	24 hr. (24 hr. at 225° C Baking)	No cracks
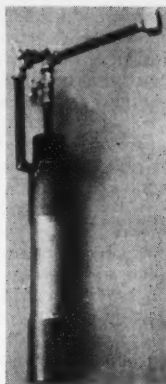
Figure 2—Type B cathode of Grade M steel (See table 3) for cathodic protection under stress.

Figure 3—Bend test embrittlement of Grade A steel (See table 2, Sec. 4) due to reduction of millscale. Magnification 4X.
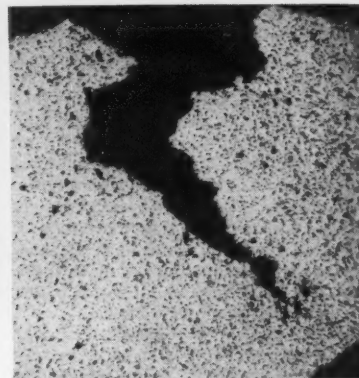
Figure 4—Crack in bend test specimen of Grade A steel (See Fig. 3) magnification approximately 37X.

which was the maximum capacity of the bending jig.

The bend test of ring sections cut from the pipe represents deformation transverse to the rolling direction and thus a different ductility than that given in Table 1 for bursting tests in which both transverse and longitudinal ductility are involved. The transverse, bend ductility of Grade B steel is less than for Grade A steel as indicated by the loads sustained at maximum bend of ring sections without crack formation. This is in contrast with values in Table 1 where Grades A and B have practically the same ductility. The transverse ductility of any rolled steel product is usually less than for the longitudinal direction unless a considerable amount of cross rolling is done.

The calibration bend tests, while they treat the sample material in an unlike manner, did produce similar bend test results in that they described a limiting bend angle. Any embrittlement factors introduced in the cathodic protection program were expected to produce cracking when the ring sections were subjected to the calibration test conditions.

Data for all tests made on cathodically protected, assembled cathode rings are given in Table 2, in sections 1 to 8 of the table. In Section 9 of the table data are given for bend tests made on pipe rings of Grade A steel which had been subjected to pickling tests with arsenic present in solution. The tests for the data which are given in Section 9 of the table were designed to show that the bend tests were quantitative in determining the degree of embrittlement resulting from different levels of uptake of hydrogen. They also were designed to show the effectiveness of the baking treatment

of 24 hours at 225 C in restoring bend ductility by removal of hydrogen.

The sponsor of the research program was especially interested in the behavior of Grade M (N-80) steel under cathodic protection because he had a large number of gas storage bottles made of this steel under cathodic protection underground. The bottles were under internal pressure due to compressed gas and the maximum stress on the extreme outer fibers was of the order of 60,000 psi. It was decided to set up a number of laboratory cells to simulate service conditions. Acordingly cathodes were designed which could be put under internal pressure with an hydraulic system using oil and in order to accentuate embrittlement conditions, it was decided to use the maximum practicable outer fiber stress (below the yield point) and the maximum current density for cathodic protection.

Six cells were set up to represent three conditions of cathodic protection thus making three duplicated tests. The test conditions were:

Series A—Cathode surface resulting from a normalizing heat treatment after hot rolling.

Series B—Cathode surface machined to remove all scale and subsurface effects of oxidation during normalizing heat treatment. Figure 2 shows the arrangement of such a cathode fully welded to a central, heavy-wall pipe and to ⅛ inch pipe to provide the internal pressure.

Series C—Cathode surface as in (a) but coated with tar-enamel coating by same procedure as practiced for the gas storage bottles.

All of the cathodes were connected to a manifold system which permitted each individual cathode to be brought to the desired pressure then shut off from the

manifold by means of the high pressure valves at each cathode. This arrangement permitted periodic inspection of each cathode for failure during the test by evidence of loss of pressure and also permitted one hydraulic system to service all six of the cathodes.

It was determined that it would be safe practice to limit the hydraulic system to a maximum pressure of 5000 psi and the maximum stress at the outer fibers of the cathodes to 77,000 psi. The latter was about 17,000 psi above the similar stress for the gas storage bottles and within about 13,000 psi of the yield point of the N-80 steel. In order to obtain this stress at the cathode surface the cathodes under Series A or C above were machined on the inside diameter to provide a nominal wall thickness of 0.078-inch. The cathodes under Series B above, which did not require the preservation of the normalized surface, were machined on the OD to a nominal wall thickness of 0.070-inch.

All of the cathodes were placed under continuous cathodic protection at a potential of —1.20 volt to the copper half cell for a period of 10 months while maintaining an internal pressure of 5000 psi to give the desired outer fiber stress of 77,000 psi. Near the end of the 10-month period one of the cathodes of Series A lost pressure due to failure of a weld which had been made to attach the pipe section cathode to the pressure assembly. All of Series A and C cathodes had been so welded because the difficult machining of the ID placed a limitation on the length of pipe section which could be used. At the end of the 10-month period of cathodic protection under stress the surviving five specimens were subjected to bursting tests with internal oil

TABLE 3—Results of Destructive Tests

Series	Call No.	Maximum Pressure (lb)	Maximum OD (Inches)	Average Thickness (Inches)	Maximum Stress (psi)	Remarks
A	13	7800	2.438	0.0748	127,000	Weld failure
A	14	No Test	.....	.....	.....	Weld failure
B	15	7700	2.172	0.0595	140,500	Burst in center
B	16	8100	2.191	0.0705	125,800	Did not fail
C	17	7200	2.401	0.0725	119,800	Weld failure
C	18	7200	2.436	0.0716	122,400	Weld failure
Prototype Control Specimen		9200	2.217	0.0705	144,500	Burst in Center

pressure immediately upon removal from the cells. Data from these tests are given in Table 3.

3. Discussion of Data

The different transverse strength and ductility of steels of Grades A, B and M and the different wall thickness of Grade M indicates why the calibration bend tests on ½ inch wide rings cut from the as-received pipe could not be made under uniform conditions. Separate calibration established the limits of bend angle and load for each material before cathodic protection was applied.

The data given in Table 2 show the initial hydrogen content and those resulting from cathodic protection under the conditions described in the table. The data for hydrogen contents are the least consistent data in the tabulation and reflect the need for equipment for analysis close at hand for convenient calibration rather than the remote facilities which were used. The table also gives average values for the bend test embrittlement observed for the four ring sections taken directly from the cathodic protection cells and subjected to the bend test.

The first evidence of embrittlement in the bend test was indicated for tests in Section 4 of the table for Grade A and B steels overprotected for a period of four months. The hydrogen contents were less than those in the unprotected pipe material. The data indicated that embrittlement had occurred as a result of cathodic protection but that the embrittlement was not a result of hydrogen uptake. It was noted that all of the rings involved in Section 4 of the table could be washed practically free of the mill scale on the cathodically protected surfaces in the vicinity of the region of maximum deformation in the bend test. It was apparent that the combination of excessive cathodic protection and deformation beyond the yield point provided minimum adherence of the initially present mill scale.

A metallographic examination was made of rings of the three grades of steel in Section 4 of the table. The examination included portions of the rings in the vicinity of maximum bend deformation and portions of rings which had been cathodically protected but not subjected to bend testing. As a result of the examination it was observed that the excessive cathodic protection had changed the character of the inner layer of scale adjacent to the base metal, which probably had an FeO composition, but the outer scale layer of Fe_3O_4 was unchanged. The reduction of FeO of the inner scale to Fe by the cathodic hydrogen was considered to be involved. Moreover the two grades, A and B steels had numerous sites of rolled-in scale and grain boundary scale penetration from which cracks were initiated during bend testing. Grade M steel however had a smooth base metal surface without scale penetration and did not suffer embrittlement even though the mill scale was loosened by the excessive cathodic protection.

The embrittlement of Grades A and B

steel under the conditions described in Section 4 of Table 2 is believed to be due to high stress concentration at sharp notches formed when FeO usually present on the metal surface lost its adherence due to excessive cathodic protection. The appearance of the cracks in the region of maximum bend test deformation of Grade A steel is shown in Figure 3 as referred to Section 4 of Table 2. At higher magnification one of the cracks is as illustrated in Figure 4. It is to be noted that the cracks which are initiated by surface notches do not propagate across the entire specimen section. The embrittlement cited above and produced by reduction of FeO was found to be of a lower order of severity than in specimens for which positive evidence of hydrogen absorption was found. Due to factors peculiar to the processing of Grade M (N-80) steel or its oxidation behavior the material represented a notch-free surface and thus was unembrittled. Subsequent metallographic examination of pipe rings represented in Section 2 and 3 of the table indicated that the completeness of reduction of the FeO portion of the mill scale varied with the current density.

It is considered probable that if cathodic protection had continued for a longer time for pipe rings in Section 2 and 3 of the table they might also have exhibited similar embrittlement due to reduction of FeO.

The above-cited embrittlement which can be called "geometric embrittlement" was an unexpected phenomenon because it occurred with no evidence of hydrogen uptake of the base metal. Several questions arose as the result of the above data; viz.: Does the presence of reducible FeO merely delay hydrogen embrittlement? If cathodic protection is carried out over an extended period to exhaustion of reducible FeO is hydrogen embrittlement then superposed on geometric embrittlement?

An attempt to partially answer these questions is provided in Sections 7 and 8 of Table 2 by cathodically protecting rings of Grade A steel from which the mill scale had been removed completely by machining below the depth of any rolled-in or grain boundary mill scale. The test data indicate that the steel A was embrittled by hydrogen absorbed during cathodic protection under the conditions cited in Section 7 and 8 of the table.

Sections 5 and 6 of Table 2 also show positive evidence of hydrogen uptake and embrittlement of steels A and B due to a combination of geometric and hydrogen embrittlement. The tests for Sections 5 and 6 were carried out with the mill scale left on and under the conditions of low initial pH. Tests for Section 6 had additionally a sulfide contamination which is seen to be a most severe embrittlement condition because the bend tests indicated embrittlement after only two months of cathodic protection.

Outstanding data in Table 2 are those showing that Grade M steel (N-80) was not embrittled under any conditions of

the tests. It is also seen that steel A had the maximum sensitivity toward embrittlement and that steel B may be embrittled under certain conditions but had a considerably lower sensitivity than steel A.

Permeation tests were made on thin cathodes of Grade M steel in order to obtain additional confirmation of the low sensitivity of this steel to embrittlement by hydrogen. The cathode used had a thickness of 0.0055-inch and was arranged in a cell so that one side acted as cathode while the other side was part of a liquid system using silicone oil in which the volume of any hydrogen transferred through the steel membrane could be measured. During two weeks of operation under the following conditions no hydrogen had diffused through the M steel cathode.

(a) pH ⅞ and potentials of —0.85 and —1.32 volt to copper half cell.
(b) pH 2.5 and potential of —0.85 volt to copper half cell.

With the low pH of 2.5 cathodic hydrogen could, however, be transferred through the steel membrane when a potential of —1.32 volt to copper half cell was maintained with a current density around 1000 ma per sq. ft. Because such high current values are extremely unlikely under normal cathodic protection conditions, the permeation tests indicate that the M steel would not be embrittled by hydrogen during cathodic protection unless the environment had a low pH and required excessive current.

The pilot tests of the three steel grades which are reported in Table 2 indicated that steel M under certain conditions of cathodic protection could absorb hydrogen but was not embrittled when deformed in a bend test. The indications were that there was no loss of ductility due to cathodic protection but since the cathodic protection was carried out with practically no applied stress the unanswered question of static fracture under cathodic protection remained.

Table 3 gives data for Grade M steel cathodically protected while under internal stress over a period of 10 months. During the testing period a failure occurred in one of the Series A specimens. However the failure was due to a welding defect and the site of the failure had been blanked off and did not have access to the electrolyte or the cathodic protection. The data in Table 3 show that the welds in Series A and C specimens were of insufficient strength to permit the full strength of the Grade M steel cathode to be realized. However the indicated maximum stress is within 15,000 to 20,000 psi of the maximum stress sustained by the prototype specimen which had not been subjected to cathodic protection.

The one Series B specimen cathode which it was possible to test destructively is shown to be within 4000 psi of the control. The tests therefore indicate that for the heat of N-80 steel under test there was no static failure during 10 months of excessive cathodic protection under stress. The destructive tests also

indicated that there was no serious loss of strength or ductility as a result of cathodic protection under stress. As far as the underground gas storage bottles were concerned the sponsor considered that the data had provided a "complete and satisfactory answer" to the question of cathodic embrittlement of the N-80 steel.

The negative data respecting the embrittlement of N-80 steel under stress confirmed the previously made pilot tests on bend specimens of cathodically protected ring sections of the same steel which also showed absence of embrittlement.

Tests of Grade M (N-80) steel were of value in relieving the sponsor of any anxiety concerning embrittlement during cathodic protection. However, Grades A and B steels are used to a wider extent than Grade M. So it is considered important that the research be extended to these steels to determine their susceptibility to failure during cathodic protection under stress. It also would be desirable to test additional specimens of Grade M steel from a number of different heats in order to check the low embrittlement sensitivity found in the material from one heat.

4. Summary and Conclusions

Ring specimens of as-hot-rolled pipe of API Grades A, B and M were cathodically protected for various periods under different conditions of cathodic protection. Bend tests were then made at low temperature to detect evidence of any change in bend ductility. Evidence of hydrogen uptake during cathodic protection was determined from vacuum fusion tests.

Of the first three conditions of cathodic protection employed described in Sections 2, 3 and 4 of Table 2 there was evidence of reduced bend ductility for steels of Grades A and B overprotected at a potential of −1.32 volt to Cu/CuSo$_4$ (current density 10-20 ma per sq ft.) for a period of four months. The reduced bend ductility was associated with the formation of notches at the metal surface due to reduction of the FeO portion of the mill scale by cathodic hydrogen. There was however no evidence of hydrogen uptake by the base metal. The

loosening of mill scale by reduction of the FeO layer also occurred to a lesser extent for the other two conditions of cathodic protection namely −0.85 volt to Cu/CuSO$_4$ (½ ma per sq. ft.) and constant current of 1 ma per sq. ft. described respectively in Sections 2 and 3 of Table 2. It was therefore considered that over a longer period of cathodic protection at a low current density "geometric embrittlement" would prevail as in the case of excessive overprotection over a 4-month period.

Data on Grade A steel in Section 7 of Table 2 show that when the mill scale was removed there was some evidence of embrittlement due to hydrogen uptake for cathodic protection for five months at a potential of −0.85 volt to Cu/CuSO$_4$. These data would indicate that the presence of reducible FeO in the mill scale delayed embrittlement which might have occurred due to hydrogen uptake in Sections 2, 3 and 4 of Table 2.

Sections 5 and 6 of Table 2 give data on embrittlement for cathodic protection under conditions which are not usually met in soils. However, even in the case of the low initial pH of 2.5 (which increased to 3.5 at the end of the test) for Section 5 of Table 2 the level of embrittlement was not as high as for the condition of excessive overprotection as in Section 4 of Table 2. The most embrittling condition of cathodic protection with low pH and sulfide ions was as described in Section 6 of Table 2. If it had been possible to carry protection on these specimens for a longer time than two months it is probable that steel M would also have been embrittled.

The condition of low pH and high sulfide concentration could be present in marsh soil wet with brackish water or in the presence of sulfate reducing bacteria. Such conditions would, according to the experimental data, practically assure the embrittlement by hydrogen of any cathodically protected steel.

The data obtained appear to warrant the following conclusions.

1. The presence of a reducible material such as FeO of the mill scale delays the uptake of hydrogen by the base metal during cathodic protection in the absence of sulfide ion contamination.

2. In the presence of sulfide ions and low pH, reduction of FeO of the mill scale and hydrogen uptake of the base metal may occur simultaneously during cathodic protection.

3. The removal of FeO from the base metal surface by reduction due to hydrogen during cathodic protection may produce embrittlement in bend tests of certain steels as a consequence of geometric or notch effects. The certain steels are those in which during hot rolling the mill scale has penetrated grain boundaries or was rolled into the surface.

4. The removal of mill scale before cathodic protection permitted uptake of hydrogen to occur in steel of Grade A under normal conditions of cathodic protection. The normal conditions of cathodic protection are considered as follows: soil pH 7-8 and potential of −0.85 volt to copper half cell with a current density around 0.5 ma per sq. ft.

5. For the three grades of steel pipe used in the cathodic protection program the embrittlement sensitivity decreased in the following order: Grades A, B to M. The M steel was not embrittled under any test conditions employed.

6. For the one steel, Grade M which was placed under cathodic protection while stressed to near-yield point level there was no evidence of static failure in ten months of excessive cathodic protection. The destructive tests made on the specimens also indicated no appreciable loss of strength or ductility resulted from such cathodic protection.

Some Platinum Anode Designs
for
Cathodic Protection
of
Active Ships*

By H. S. PREISER and B. H. TYTELL

Abstract

Voltage-current relationships have been determined for platinum wires, gauze and disc and a platinum-clad tantalum disc, in sea water tests in the laboratory and in Boston harbor.

The platinum-clad tantalum disc produced the best current-voltage ratio. In the range of 5 to 18 volts in the harbor tests, 2.0 amperes were obtained per impressed volt. The other anodes gave 1.3 amperes per impressed volt in the harbor tests. In the laboratory tests, the ratios obtained were 3.2, 3.1, 2.6, 2.2, and 2.1 amperes per volt for the platinum-clad tantalum disc, wire gauze, 48-inch wire spiral, 36-inch wire spiral and the flat disc, respectively. 5.2.3

Introduction

CATHODIC protection of active ships has been undergoing rapid developments in the past ten years.[1] The development of special aluminum and magnesium alloys as galvanic anode materials and the discovery of adverse effect of iron in concentrations higher than 0.0014 percent on the performance of zinc as a galvanic anode led to widespread use of these materials in the cathodic protection of ocean going ships.[2,3,4] Such sacrificial anode systems are self-contained sources of current that are easy to install and with the exception of magnesium do not require any controls.

However, because of the limited current output per unit area of galvanic anodes, large numbers must be used even for such ships as destroyers to provide sufficient current for their protection.[5] The current potential per pound of galvanic anodes makes it necessary also to use large bulks to provide sufficient current for 18-24 month periods between drydockings even under normal conditions. If a ship bottom suffers large scale paint damage, demand on the anodes for protection is high and they are used up rapidly, leaving the ship without protection long before it is scheduled to be drydocked.

From an economic standpoint too, galvanic anodes are an expensive source of current. Zinc requires 26 lb per ampere year, magnesium 17 lb and aluminum 12 lb. The cost per pound of Zinc is 20c, that of magnesium 38-40c and that of aluminum is 65c. This primary materials cost is compounded further by the labor cost associated with renewal of anodes. In spite of these obstacles, their inherent advantages of relative simplicity of installation and self-containment of power source make galvanic anode systems attractive for many applications.

Impressed current or externally energized anode systems always have had wide appeal for cathodic protection applications because of their versatility and relative permanence, but until recently, available anode materials have had one deficiency or another precluding their large-scale adoption. The decided advantage of having readily controlled

★ Submitted for publication Dec. 31, 1958. A paper presented at a meeting of National Association of Corrosion Engineers' Northeast Region, Boston, Mass., October 6-8, 1958.

high-current output from a few light-weight streamlined anodes, has encouraged solution of other difficulties associated with the use of energized anodes.

Review of Anode Materials

Much work in the electroplating and allied electrochemical process field in the past two decades has paved the way for the adaptation and improvement of anode materials for impressed current cathodic protection systems. For example, from the electrolysis of brine for chlorine production came the use of impregnated graphite, which quickly found application in the cathodic protection of underground piping systems.

Graphite anode systems have been installed on a limited scale aboard ship but in order to make their use practical, special holders had to be designed to overcome their fragility.[6,7,8,9,10] Even when using these innovations, graphite has a definite, but relatively low ampere-hour weight loss, and its large size presents difficulty for streamline fitting to a ship hull.[11]

Steel anodes for impressed current systems have been used with success, but like other highly soluble anodes, they are large, heavy and are consumed rapidly.[12]

High silicon iron has shown promise for certain impressed current applications; however, its use in fresh water appears to be more advantageous than its use in sea water. High silicon iron is attacked readily in sea water electrolytes by chlorine anode reaction products.[11]

Lead anodes containing silver and possibly other alloys have been suggested in the literature as an inert anode material.[13,14] The low rate of electrochemical deterioration associated with lead, combined with its excellent mechanical properties have resulted in some recent shipboard installations of this promising material.[15]

Advantages of Platinum

Of all the anode materials thus far considered, none can approach the electrochemical and physical properties of platinum. Platinum and alloys of platinum are well known materials in the electroplating, electrochemical process and electrochemical analytical fields. These materials have the desirable properties of chemical inertness, excellent electrical conductivity and mechanical workability. The high cost of these pre-

Preiser   Tytell

HERMAN S. PREISER is a consulting corrosion engineer in charge of cathodic protection for the Research and Development Division of the U. S. Navy Bureau of Ships. He has a BS degree from Webb Institute (1949). Mr. Preiser has been active in NACE affairs since 1948 and was Technical Program Committee Chairman for the 1959 Northeast Regional Meeting. He has contributed profusely to the corrosion literature and he holds several patents related to shipboard cathodic protection systems.

BORIS H. TYTELL is a research chemist in charge of the Research, Development and Consulting Section of the Chemical Laboratory at the Boston Naval Shipyard. He has been intimately concerned with marine corrosion problems since he entered government service in 1930. He received his BS in chemistry in 1921 from Brooklyn Polytechnical Institute and spent two additional years pursuing graduate studies there. He is an active member of The Electrochemical Society, National Association of Corrosion Engineers and The Society of Plastic Engineers. He is author of many articles on cathodic protection and has recently been granted a patent on a new type of anode holder.

cious metals, which once was a factor in limiting their use to very specialized applications, has been overcome largely by cladding or plating thin layers of platinum over less expensive basis metals.

Several attempts have been made to design practical shipboard cathodic systems using platinum-clad anodes.[1,16,17,18] In fact, one cathodic protection system utilizing platinum foil circular anodes has been marketed commercially.[19]

The serious drawback of platinum-clad material prior to relatively recent developments, was that a pore-free cladding had to be applied over common basis metals, such as silver and copper, in order to prevent their electrochemical deterioration. Sealing the edges of clad silver and copper was also troublesome. Silver was thought to be a better choice of basis metal because of its relatively slower solubility when electrolyzed to silver chloride in sea water.

Figure 1—Platinum-clad copper rod 2 x ¼-inch D mounted in melamine holder.

Figure 2—Deterioration of melamine holder after one year's service.

Figure 3—Platinum-clad silver rod mounted in a ceramic coated steel holder.

Figure 4—Reinforced plastic holder for housing 52 x ¼-inch D platinum-clad silver rod anode.

Figure 5—Hull-mounted flush type circular platinum clad foil anode. (Top View.)

Figure 6—Same as Figure 5, side view.

The commercial introduction of "rectifier," metals such as tantalum and titanium has led to the important development of platinum-coated anodes of these materials. Tantalum and titanium exhibit an interesting property when electrolyzed in sea water or aqueous acid media. An insulating oxide is formed on the surface which gradually increases in electrical resistance until current can no longer pass into the electrolyte.[21, 22] The oxides of titanium formed in sea water and stable neutral chloride solutions are insulating up to about 12 volts applied across the film.[23, 20] Increasing the voltage above 12 volts causes the insulating oxide to rupture and electrochemical solution of the metal occurs.[23] The oxides of tantalum formed in acid media are stable up to 130 volts forming and reforming at characteristic voltage levels up to the maximum.[24]

The combination of platinum cladding or plating on titanium and tantalum has resulted in a low-cost anode which can pass high-current densities without deterioration of the basis metal.[23] These platinum coatings no longer depend on continuity or have to be pore-free to perform. The low electrode-electrolyte interface resistance between platinum and sea water permits the stable oxide to form on the supporting tantalum or titanium because the voltage across the oxide film is kept within safe limits. Several patents relating to the use and fabrication of clad titanium and tantalum have been issued during the past two decades.[25, 26, 27, 28] Recent advances in the inexpensive commercial production of tantalum and titanium combined with ingenious ways of applying thin layers of platinum over them has made these inert anode materials instantly available.

Early Navy Experience

Early Navy experience with clad platinum anodes dates back to 1952. A copper rod ¼ diameter by 2-inch length, clad with a 5-mil platinum coating, was mounted in a plastic holder as shown in Figure 1. About 10 anodes were mounted on the hull of a submarine and con-

nected to an internal DC power source. Painted vinyl shields, 20 mils thick, extended out on the hull under each anode for a radius of about three feet. It was obvious, after installation, that the driving voltage to produce substantial protective current would be excessive so the ship was operated at reduced capacity for almost one year. Some damage to the vinyl shields occurred and the melamine plastic holder deteriorated by attack from the oxychloride anode reaction products.[17] See Figure 2. It was realized from this experience that suitable anode design would have to consider geometry and mountings as prime factors affecting permanence and performance.

The next logical development was to lengthen the platinum-clad rods to reduce their sea path resistance and mount them in more chemically resistant holders. A 52-inch by ¼-inch rod was mounted in a steel holder as shown in Figure 3. Insulation was provided by a coating on the holder. Rubber coatings tried first proved to be inadequate and ceramic coatings tried next also suffered stray current damage through the pores in the coatings after about one year's service. Finally, for long rods, an all-plastic holder was designed using reinforced epoxy and polyester resins[29] as shown in Figure 4. The resistant properties of these anode holder materials caused them to be used in future anode designs. Work on improved materials for dielectric shielding of the hull in the vicinity of the anode has had to keep abreast of anode improvements.[30]

The demand for streamlined anodes for high-speed ships prompted the design of flush-type circular anodes of ogival cross-section as shown in Figures 5 and 6. Although this change in geom-

etry resulted in a higher anode-to-sea path resistance, the superior mechanical features far outweighed the minor electrical disadvantage.

Design Criteria

The principal characteristics to be considered in suitable hull-mounted anode designs for active ships are listed below:

1. High current output at low-impressed voltage;
2. Geometric shape consistent with above current requirements, streamlining and ease of mounting:
3. Mechanical properties of compactness, strength and ability to be fabricated readily;
4. Electrical properties of good conductivity and of ease of connecting to a power source by suitable leads;
5. Electro-chemical properties of low solubility and non-formation of resistant films under electrolysis.
6. Availability at low cost.

Platinum anode combination materials described earlier meet the above design requirements.

The purpose of the remainder of this article is to describe some preliminary experiments related to the geometry of platinum-clad anodes and to describe the performance of a porous platinum coating clad on a substrate of tantalum.

Methods of Tests

Platinum Forms Used

Anodes were fabricated from pure platinum in the following shapes:

Flat disc—7-inch diameter, 0.005-inch thick;

Wire Gauze—7-inch diameter, 0.007-inch thick (45 mesh);

Wire Spiral—37-inch long, 0.063-inch diameter wire;

Wire Spiral—48-inch long, 0.063-inch diameter wire (See Figure 7).

In addition to these a tantalum disc was fabricated 7-inch diameter, 0.015-inch thick, clad with a platinum coating 0.001-inch thick. (See Figure 8.)

Experimental

Figure 9 shows the laboratory set-up used to establish voltage-current relationships for the anodes. The unpainted steel interior of a 55-gallon drum served as the cathode. Each anode tested was mounted in a plastic holder, with a suit-

Figure 7—Platinum wire spiral anode, using 48 inches of 0.063-inch D wire.

Figure 8—Platinum-clad tantalum 7-inch D disc, showing embossed surface.

Figure 9—Laboratory setup for establishment of voltage-current relationships of various platinum anodes.

able lead wire insulated at the junction. The electrolyte was sea water taken from Boston harbor.

The voltage was varied from 0 to 18 in steps of one volt, allowed to remain at each voltage for five minutes and the corresponding current output noted.

These experiments were repeated in Boston harbor, using a ship's hull as a cathode. Each anode was mounted on a weighted board and lowered five feet into the sea, over the side of the vessel.

Results of Tests

Tables 1 and 2 for laboratory and Boston harbor immersion tests respectively show the current obtained with various anodes, with impressed voltages from 2 to 18 volts. Data from these tables are shown in graphical form in Figures 10 and 11.

Tables 3 and 4 show the current-voltage ratios for various anodes in the range of 5 to 18 volts. In this voltage range, the current-voltage ratios are linear. It will be noted that the platinum-clad tantalum disc produced the best current-voltage ratio. In the harbor tests, 2.0 emperes were obtained per impressed volt with this anode, whereas the other anodes gave 1.3 amperes per

volt. In the laboratory tests, the ratios obtained were 3.2, 3.1, 2.6, 2.2 and 2.1 amperes per volt for the platinum-clad tantalum disc, wire gauze, 48-inch wire spiral, 36-inch wire spiral and the flat disc respectively.

Resistance of Anodes

Before discussing the performance of the anodes it will be well to review methods of determining their electrolytic resistance. Several theoretical and empirical mathematical treatments on calculating the resistance of anodes have appeared in the literature. The following brief description on the electrolytic resistance of vertical and horizontal rods to ground has been abstracted from an article "Design of Anode Systems for Cathodic Protection of Underground and Water Submerged Metallic Structures"; *Corrosion*, **6**, 360-375 (1950) Nov.

Rods

For long vertical rods where the ratio length, L, to diameter, a, is 100 or over, the resistance to radial flow of current is given by:
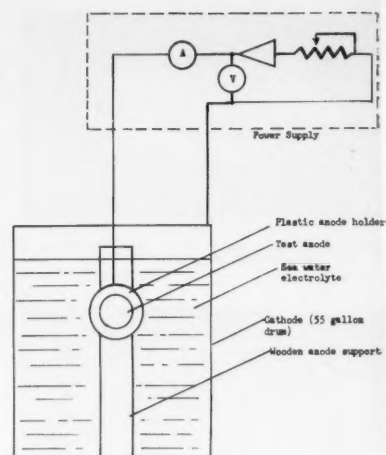
$$R = \frac{0.012 \, \rho \, \log_{10} D/a}{L} \quad (1)$$

R = seapath resistance, ohms
ρ = water resistivity, ohm-cm
D = distance from anode, feet
a = diameter of rod, feet
L = length of rod, feet

Since resistance increases logarithmically with distance from anode, let us arbitrarily fix the remote distance at D/a = 500 therefore formula (1) can be further simplified to:

$$R = \frac{0.0324}{L} \rho \quad (2)$$

TABLE 1—Current Output At Various Impressed Voltages
Laboratory Tests
Current Output in Amperes*

Impressed Volts	Flat Disc	Wire Gauze	Wire Spiral 36-Inch	Wire Spiral 48-Inch	7-Inch Platinum-Clad Tantalum
2	1.0	1.0	1.0	2.0	0.5
3	2.5	2.0	2.5	3.0	2.5
4	4.0	4.0	4.5	5.0	5.0
5	6.0	7.0	7.0	8.0	7.5
6	8.0	10.5	9.0	10.0	10.0
7	10.0	13.0	11.0	13.0	14.0
8	12.0	16.0	14.0	16.0	16.5
9	14.0	19.5	16.0	18.0	20.0
10	16.5	22.0	18.5	22.0	24.0
11	19.0	25.0	20.0	24.0	27.0
12	21.0	28.0	23.0	27.0	30.0
13	23.0	31.5	25.0	29.0	34.0
14	26.0	35.0	27.5	32.0	38.0
15	28.0	38.0	29.0	35.0	40.0
16	30.0	41.0	31.0	38.0	44.0
17	33.0	44.0	33.0	40.0	47.0
18	35.0	47.5	35.0	42.0	50.0

* = Average of four measurements.

TABLE 2—Current Output At Various Impressed Voltages
Boston Harbor Tests
Current Output in Amperes*

Impressed Volts	Flat Disc	Wire Gauze	Wire Spiral 48-Inch	Platinum-Clad Tantalum Disc
2	0.5	0.5	0.5	1.0
3	1.0	1.0	1.0	2.0
4	2.0	2.0	2.0	4.0
5	3.0	3.5	3.0	6.0
6	4.5	5.0	5.0	8.0
7	5.5	6.0	5.5	9.75
8	7.5	7.0	7.0	11.50
9	8.5	8.5	8.0	13.5
10	9.5	10.0	9.0	15.5
11	10.5	11.0	10.5	18.0
12	12.5	12.5	12.0	20.0
13	13.0	14.0	13.0	22.0
14	15.0	15.0	14.0	24.5
15	16.0	16.5	16.0	26.5
16	17.5	17.5	17.0	28.0
17	19.0	19.5	18.0	30.0
18	20.0	20.0	20.0	32.5

* = Average of four measurements.
Sea Water Characteristics:
Average Temperature........60 F
Specific Resistance, 60 F.....27 to 30 ohm-cm
pH (85 F)................. 7.1 to 7.6
Dissolved Oxygen.......... 4.8 ppm
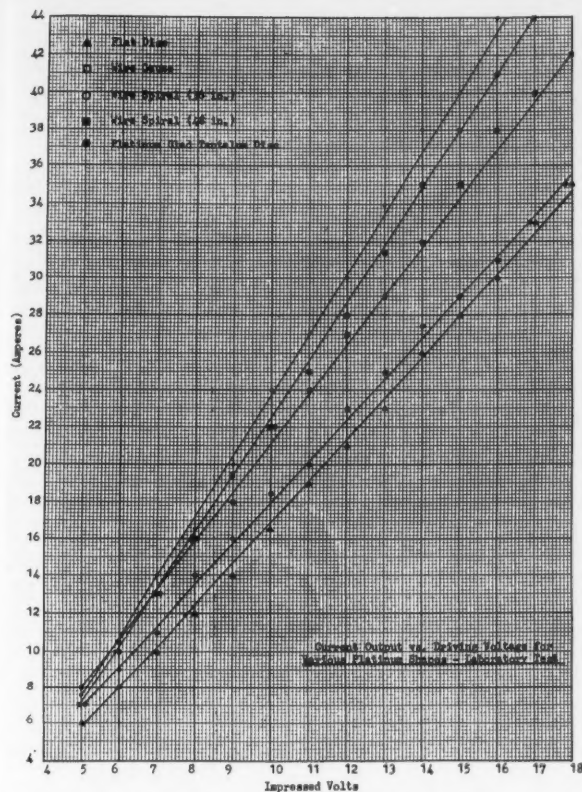
Figure 10—Current output vs driving voltage for various platinum shapes, laboratory test.
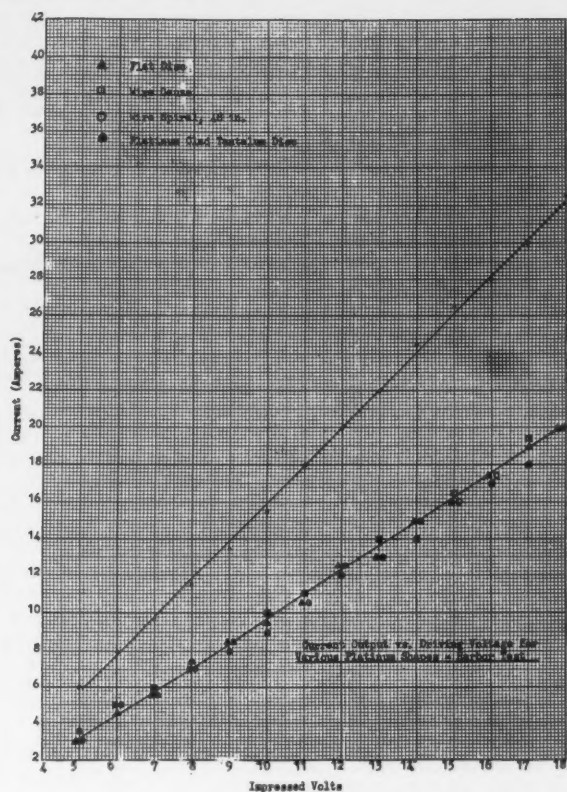
Figure 11—Current output vs driving voltage for various platinum shapes, harbor test.

Where short rods are used whose L/a is less than 100 then equation (1) or (2) must be multiplied by a factor, A, plotted in Figure 12.

Where rods are horizontal instead of vertical, then equation (1) or (2) must be multiplied by a factor, B, plotted in Figure 13.

Where horizontal rods are short, L/a is less than 100, then equations (1) or (2) are multiplied by factors A and B.

Examples

Now calculate the resistance of several anode shapes and compare them to the measured values as illustrated in Table 5.

Discs

Where a circular plate is immersed to a depth greater than radius of plate, the resistance for one side of the plate is given by:[32]

$$R = \frac{\rho}{4r} + \frac{\rho}{4\pi d} \qquad (3)$$

R = seapath resistance, ohms

ρ = water resistivity, ohm-cm

r = radius of disc, cm

d = depth of disc submerged, cm

This formula is applicable to mesh screens and other circular configurations made up of spiral wires, grids that are closely spaced, except that where all anode surfaces are exposed the above resistance is multiplied by a factor C of 0.5. The proximity of an insulating mounting holder will cause the factor C to vary between 0.5 and 1.0.

TABLE 3—Current-Voltage Relationship From 5-18 Volts
Laboratory Tests
Amperes Per Volt*

Impressed Volts	Flat Disc	Wire Gauze	Wire Spiral 36-Inch	Wire Spiral 48-Inch	7-Inch Platinum-Clad Tantalum
6	2.0	3.5	2.0	2.0	2.5
7	2.0	3.0	2.0	2.5	3.3
8	2.0	3.0	2.3	2.7	3.0
9	2.0	3.1	2.3	2.5	3.1
10	2.1	3.0	2.3	2.8	3.3
11	2.2	3.0	2.2	2.7	3.3
12	2.1	3.0	2.1	2.7	3.3
13	2.1	3.1	2.3	2.6	3.3
14	2.2	3.0	2.3	2.7	3.3
15	2.2	3.1	2.2	2.7	3.3
16	2.2	3.1	2.2	2.7	3.3
17	2.3	3.1	2.2	2.7	3.3
18	2.2	3.1	2.2	2.6	3.3
Average	2.1	3.1	2.2	2.6	3.2

*—Calculated from data from Table 1, using the slope between 5 and 18 volts.

Example: for the flat disc at 18 volts:

$$\frac{35 \text{ amps}-6.0 \text{ amps}}{18 \text{ volts}-5 \text{ volts}} = 2.2 \text{ amperes per volt}$$

TABLE 4—Current-Voltage Relationship From 5-18 Volts
Boston Harbor Tests
Amperes Per Volt*

Impressed Volts	Flat Disc	Wire Gauze	Wire Spiral 48-Inch	Platinum-Clad Tantalum Disc
6	1.5	1.5	2.0	2.0
7	1.3	1.3	1.3	1.9
8	1.5	1.3	1.3	1.8
9	1.4	1.3	1.3	1.9
10	1.3	1.3	1.2	1.9
11	1.3	1.3	1.3	2.0
12	1.4	1.3	1.3	2.0
13	1.3	1.3	1.3	2.0
14	1.3	1.3	1.2	2.1
15	1.3	1.3	1.3	2.1
16	1.3	1.3	1.3	2.0
17	1.3	1.3	1.3	2.0
18	1.3	1.3	1.3	2.0
Average	1.3	1.3	1.3	2.0

*—Calculated from data from Table 2, using the slope between 5 and 18 volts.

Example: for the flat disc at 18 volts:

$$\frac{20 \text{ amps}-3 \text{ amps}}{18 \text{ volts}-5 \text{ volts}} = 1.3 \text{ amperes per volt}$$
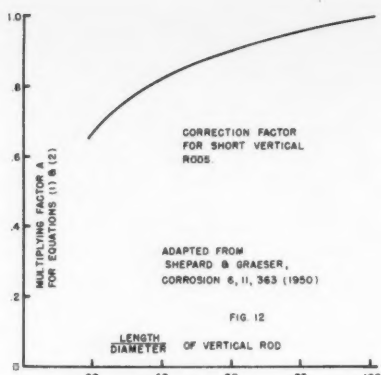
Figure 12—Plot of correction factor for short vertical rod.

Figure 13—Plot of correction factor for changing vertical rod formula to horizontal rod.

Figure 14—Platinum-clad tantalum circular anode assembly, schematic cross-section.

Discussion

It can be seen that when the distance to cathode is small relative to the anode radius as in the laboratory tests, there is a definite decrease in the resistance values of the anode when compared to those values measured in the open sea water tests. The change in resistance is also influenced by the small cathode size, degree of aeration of the electrolyte and cathode polarization. It is interesting to note that the other anode shapes such as the mesh, 48-inch spiral and 36-inch spiral all showed lower resistances than the single side of the flat disc indicating that some part of the opposite face of the anode in question was contributing to current output. This means that the value of factor C is between 0.5 and 1.0 when used in combination with Equation (3). The major decrease in resistance was observed for the embossed platinum-clad tantalum suggesting possible surface reduction of resistance above that which can be attributed to its geometric shape or its metallic internal resistance.

In the harbor tests the resistances of the various anode configurations, except the platinum-clad tantalum, were about equal. This is understood when one considers that the opposite face of the exposed anode mesh and spirals did not contribute as much current as in the laboratory tests because the ratio of distances between anode face to cathode and the opposite anode face to insulating mounting is so much greater. Therefore the anode presents a somewhat similar geometric-shaped single-faced disc to the cathode. However, the platinum-clad anode maintained an even lower resistance than the general disc geometry would indicate, showing a similar reduction in surface resistance as observed in the laboratory tests. A small part of this lower resistance can be attributed to a lesser metallic resistance due to a greater disc thickness and the remainder may be attributed to the ready release of anode reaction gases because of the embossing and inherent porosity of the platinum cladding.
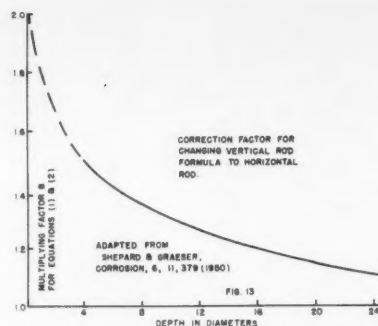
Conclusions

From the preliminary studies conducted, platinum-clad tantalum anodes appear to have superior resistance (lower) characteristics over that of a solid plate, mesh or open spirals. Platinum-clad titanium should be expected to perform similarly. These materials are inexpensive and are the logical choice for anode applications in cathodic protection designs. A schematic cross section of an anode holder assembly suitable for shipboard use is shown on Figure 14. This drawing delineates the anode design shown in Figures 5 and 6.

Further Work

Weight loss characteristics of platinum-coated tantalum and titanium anodes will be studied as a function of platinum thickness and current density and method of applying the platinum coating.

The opinions expressed in this paper are the personal views of the authors and do not necessarily reflect the official views of the United States Navy.

TABLE 5—Resistivity of Boston Harbor Water is approximately 28.5 ohm-cm (P)
Anodes are remote distance to large cathode

Anode Geometry (Inches)	Formula	Calculated Resistance ohms	Measured Resistance
Rod, 2 x ¼ Dia.....	(2)xAxB	3.65	...
Rod, 52 x ¼ Dia.....	(2) x B	0.232	...
Disc, one side, 3½ radius.........	(3)	0.805	0.77
Disc, wire gauze, one side, 3½ radius.........	(3)	0.805	0.77
Wire Spiral one side, 3½ radius...	(3)	0.805	0.77
Platinum-Clad Tantalum Disc, one side, 3½ radius.........	(3)	0.805	0.5

References

1. D. P. Graham, F. E. Cook, H. S. Preiser. Cathodic Protection in the U. S. Navy—Research-Development-Design. *Trans. Soc. Nav. Arch. & Mar. Eng.*, 64, 241-317 (1956).
2. K. N. Barnard. Cathodic Protection as Applied to Ships and Establishments of the Royal Navy. *Chemistry and Industry* (British), 172-182 (1954).
3. C. F. Schreiber. The Use of Magnesium for the External Cathodic Protection of Marine Vessels. *Corrosion*, 14, 126t-130t (1958) March.
4. B. H. Tytell and H. S. Preiser. Cathodic Protection of an Active Ship Using Zinc Anodes. *J. Amer. Soc. Nav. Eng.*, 68, 701-704 (1956) and *Corrosion*, 13, 515t-518t (1957) August.
5. L. J. Waldron and M. H. Peterson. The Current-Voltage Relationship of Galvanic Anode Arrays. *Corrosion*, 13, 289t-294t (1957) April.
6. K. N. Barnard, G. L. Christie and J. H. Greenblatt. Cathodic Protection of Active Ship in Sea Water With Graphite Anodes. *Corrosion*, 9, 246t-250t (1953) August.
7. F. E. Cook and H. S. Preiser. Plastics Used to Hold, Insulate Anodes for Ship Hulls. *Materials and Methods*, 46, 170-171 (1957) May.
8. H. S. Preiser and M. Stander. Plastics in Marine Cathodic Protection Systems. *Buships Journal*, 6, 17-21 (1957) March.
9. E. A. Wagner. Holder for Underwater Anode. U. S. Patent 2,776,941, issued 8 Jan. 1957.
10. J. P. Oliver. Mounting For Underwater Anode For Ship's Hull. U. S. Patent 2,776,940 issued 8 Jan. 1957.
11. S. Tudor, W. L. Miller, A. Ticker and H. S. Preiser. Electrochemical Deterioration of Graphite and High Silicon Anodes in Sodium Chloride Electrolytes, *Corrosion*, 14, 93t-99t (1958) February.
12. K. N. Barnard. Prevention of Corrosion of Ships in Sea Water (II). *Research* (British), 5, 176t-180t (1952) April.
13. C. G. Fink. Corrosion Resistant Anodes. Corrosion Handbook, edited by H. H. Uhlig, 606-609. John Wiley & Sons Inc. (1948).
14. J. H. Morgan. Lead Alloy Anodes Tested Up to 20 Amp. Sq. Ft. *Corrosion* (Technical Topics) 13, 128 and 130 (1957) July.
15. K. N. Barnard, D. G. Gage and L. G. Christie. Lead—2% Silver Alloy As An Inert Impressed Current Anode, *Corrosion*, 15, No. 11. —— 1959 (Nov.).
16. H. S. Preiser and F. E. Cook. Cathodic Protection of An Active Ship Using a Trailing Platinum Anode. *Corrosion*, 13, 125t-131t (1957) February.
17. E. E. Nelson. An Impressed Current Cathodic Protection System Applied to a Submarine. *Corrosion*, 13, 122t-124t (1957) February.
18. I. D. Gessow. Navy Experimental Work With Cathodic Protection. *Corrosion*, 12, 100t-106t (1956) March.
19. Charles Engelhard, Inc., East Newark, New Jersey, Technical Pamphlet, "The Capac System of Cathodic Protection" (1957).
20. C. D. Hall and N. Hackerman. Charging Processes on Anodic Polarization of Titanium. *J. Phy. Chem.*, 57, 262-268 (1953) March.
21. J. B. Cotton. Anodic Polarization of Titanium, *Chemistry and Industry* (British) 68-69 (1958).
22. C. A. Hample. Corrosion Properties of Tantalum, Columbium, Molybdenum and Tungsten. *Corrosion*, 14, 557-560 (1958) December.
23. J. B. Cotton. Platinum-Faced Titanium For Electrochemical Anodes. *Platinum Metals Review*, 2, 45-47 (1958) April.
24. Private communication to author on 10 October 1958 from Mr. J. Evard, Fanstell Metallurgical Corporation, North Chicago, Illinois.
25. G. Baum. Anodes For Forming Percompounds. U. S. Patent 1,477,099 issued 11 Dec. 1923.
26. A. M. Suggs, et al. Electrode for Electrochemical Oxidation. U. S. Patent 2,636,856 issued 28 April 1953.
27. P. C. Kerk. Electrode For Electrolytic Baths. U. S. Patent 1,970,804 issued 21 Aug. 1934.
28. H. W. Boessenkool et al. Solid Phase Bonding of Metals. U. S. Patent 2,691,815 issued 19 October 1954.
29. H. S. Preiser and M. Stander. Applications of Plastics in Marine Cathodic Protection Systems. *J. Amer. Soc. Nav. Eng.*, 68, 581-590 (1956) August.
30. W. J. Francis, H. S. Preiser and F. E. Cook. Cathodic Protection, Its Effect on Shipbottom Paints. *J. Amer. Soc. Nav. Eng.*, 70, 401-419 (1958) August.
31. E. R. Shepard and Henry J. Graeser, Jr. *Corrosion*, 6, No. 11, 360-375 (1950) Nov.
32. E. D. Sunde. Earth Conduction Effects in Transmission Systems. P. 75, D. Van Nostrand Company, Inc. (1949).

Any discussion of this article not published above will appear in the June, 1960 issue

The Residual Oil Ash Corrosion Problem*

*By C. J. SLUNDER**

Introduction

ALTHOUGH residual fuel oils have been used for many years for a variety of heating applications, corrosion by the ash was not considered a pressing problem until about ten years ago. In the power generation field, this coincided approximately with the advent of boilers producing 1050-1100 F steam and with the interest in mercury boilers and oil-burning gas turbines. In each of these applications, metal surface temperatures at some locations in the equipment could be expected to exceed about 1200 F. Also, the over-all yield of residual petroleum products has continued consistently downward over the past several decades,[1, 2, 3] and has resulted in greater and greater concentration of the nonvolatile ash-forming constituents in the residual heavy oil. Weber[2] has indicated that this trend will continue and this is cause for concern among designers because of the probable increase in corrosion and deposit problems.

The composition of residual oil ash varies widely,[4] and the reported analyses indicate that many elements may be found in the ash. Most of these elements are present in trace quantities only and the bulk of the ash usually consists of compounds of vanadium, iron, nickel, sulfur and the alkali metals. The compounds of vanadium, sodium and sulfur are of particular interest because of their association with deposit formation and accelerated corrosion effects at high temperatures. While the ash content of heavy fuel oil varies appreciably, depending on the source of the crude and the method of processing, it usually is not over 0.1 percent. Source of the crude determines the quantity of vanadium which will be concentrated in the ash. Reported analyses have indicated that the V_2O_5 content, in percent of total ash, can vary from a trace up to over 80. Similar variations occur in the sodium content. Also, sulfur content of crude oils has been reported in the range of 0.7 to over 5.0 percent. Behavior of these ash constituents as related to their over-all effect on high temperature oxidation has received the attention of many investigators in recent years.

General Aspects

Case histories reporting on the severity of residual oil ash corrosion have been disclosed from time to time, and a few of these have been collected in the report of NACE Task Group T-5B-3.[5] These show that both cast and wrought, heat-resistant alloys have corroded in some instances at rates far exceeding the normal oxidation of the alloys in air or flue gases. The available information indicates that the fuel oil used averaged about 0.05 percent ash of which up to 25 percent was reported as V_2O_5. Operating temperatures were usually over 1200 F. The severe tube-wastage problem encountered in the operation of a mercury boiler was described several years ago.[6] In this case, long irregular grooves about 0.040-inch in depth had been developed by corrosion on the surfaces of 5 Cr-1.5 Si-0.5 Mo furnace tubes, where the temperature was known to be over 1150 F. The boiler was fired with a Bunker-C oil containing 2.5 percent sulfur and an ash content of 0.04 to 0.08 percent. Vanadium in the ash was reported as about 40 percent V_2O_5.

Some of the early experiences in the operation of gas turbines have been described by Evans,[7] Sachs,[4] Draper[8] and others. Here again, deposition and corrosion were observed on turbine blading and nozzles when burning residual fuels high in vanadium and sodium. It was indicated by Buckland, Gardiner and Sanders[9] that firing temperatures then in use were in the range of 1300 to 1500 F. The question of deposit formation appears to be of greater concern because clogging of the turbine passages results in decreased efficiency. However, as Draper[8] points out, the problems of corrosion and ash deposition appear to be inter-related.

The foregoing practical experiences are given merely to illustrate the nature of the problems and are not intended to be a record of all previous experiences. The published literature shows that considerable additional information has been accumulated as a result of experimental work which has been done to study the specific variables involved.[10-14]

Several approaches have been considered in the study of the general problem. These include:

1. Treatment of the oil to eliminate or reduce the concentration of harmful ingredients.

2. Evaluation of known alloys and development of more corrosion-resistant alloys.

3. Evaluation of protective coatings.

4. Use of additives which combine with vanadium pentoxide to form an inert compound.

5. Design and operating changes.

6. Attempt to establish the mechanism of corrosion.

All of these approaches have received more or less attention.

In connection with the treatment of residual oil, Sachs[4] has summarized the results of a few investigations. The ash content has been reduced by centrifuging, but because vanadium is present in the oil as a soluble organic compound it

Abstract

Progress being made in combatting accelerated high-temperature corrosion caused by combustion products of residual fuel oils is reviewed. Results of laboratory investigations cannot be compared strictly because of wide differences in testing procedures used. No effective and economical method for removing all offending ash components has been found, although lowering of sodium content by washing with magnesium sulfate solution has been applied successfully to gas turbine operation. Available high-temperature alloys do not have adequate resistance to oil-ash attack at temperatures above 1200 F. Improved corrosion resistance has been attained with certain experimental alloys but some of these are difficult to fabricate into the required form and have inferior mechanical properties. Surface treatments such as aluminizing, chromizing and siliconizing appear to have some inherent protective value, but further development of procedures for applying impervious and adherent coatings is needed.

Investigation of oil additives has received the most attention in recent years. A great many inorganic, or metal-organic compounds are effective oil-ash corrosion inhibitors but only a few have been found to be economically feasible. Additives raise melting point of ash components so they will be solid at operating temperatures in boilers and gas turbines. Under certain conditions some additives reduce corrosion but increase deposit formation.

Progress is being made in basic studies to identify reactions taking place during combustion of oil and in appplication of this knowledge to establish mechanism of the corrosion reaction.   4.3.3

is not removed by this procedure. Actually, on combustion, the vanadium pentoxide is concentrated in a smaller total ash content. Filtration has been reported to have reduced the sodium content of a heavy fuel, but oil-soluble vanadium complexes were not removed. Lowering of the sodium content by washing and centrifuging the oil has been accomplished satisfactorily for gas turbine operation. Ion-exchange methods have been investigated, particularly for the removal of sodium. Under certain conditions up to 90 percent of the sodium in oil-sea water emulsions has been removed. Other methods which involve additional refining or solvent extraction are considered to be too costly and are impractical within the price limitations of residual fuel oils.

Mechanism of Corrosion

Some attempts have been made to define the mechanism by which this type of corrosion occurs so that the direction of experimental work leading to a solution of the problem could be more clearly indicated. Early workers[7, 15, 16, 17] established the fact that the presence of molten oxides or complexes was necessary to promote accelerated oxidation. Because alkali metal compounds and vanadium pentoxide often comprise a major portion of residual oil ash, much of the research interest has been focused on their behavior and chemical reactions.

Monkman and Grant[18] discussed the

effect of Na_2SO_4 in V_2O_5 — Na_2SO_4 mixtures and offered evidence that the melting point is lowered below that of V_2O_5 and also that the fluidity of such mixtures increases with increasing Na_2SO_4 content. The latter fact may help promote accelerated oxidation at temperatures below the melting point of V_2O_5. At 1300 and 1400 F, maximum corrosive attack on AISI 347 steel appeared to occur in mixtures containing about 20 percent Na_2SO_4. At higher temperatures, the authors observed that corrosion decreased with increasing Na_2SO_4 content and attributed this to a dilution effect of the corroded metal oxides.

Cunningham and Brasunas[19] amplified this work and verified that the most corrosive Na_2SO_4 — V_2O_5 mixtures were those made up to contain 15-20 percent Na_2SO_4. A maximum in the curve of Na_2SO_4 content vs corrosion appeared at that point in the temperature range of 1300 to 1650 F. This observation could not be correlated to changes in melting point, but seemed to be related to oxygen absorption in the molten mixtures. By means of pressure temperature measurements on various mixtures heated in sealed capsules in the presence of oxygen, the authors observed that oxygen absorbing capacity increased progressively as the Na_2SO_4 content was raised from 0 to 16.32 percent. Between 16.32 and 50 percent, oxygen absorbing capacity decreased slowly, and above 50 percent Na_2SO_4 very little oxygen absorption occurred. The molten mixture which dissolved the most oxygen also appeared to be the most corrosive. It was proposed that the corrosion is caused by reaction between the metal and oxygen dissolved in the molten mixture. Atmospheric oxygen passes freely through the porous oxide scale to the molten mixture at the metal-oxide interface.

Both Foster, Leipold and Shevlin[20] and Hale and Starnes[21] have reported that the extremely corrosive mixture made by fusing Na_2SO_4 plus V_2O_5 in a mole ratio of 1 to 6, can be represented as $Na_2O \cdot V_2O_5 \cdot 5V_2O_5$. This compound absorbs oxygen when molten and liberates it on solidification at 1160 F.

Foster, et al.[20], as a result of phase equilibrium studies reported further that other potential corrosive compounds were $NaVO_3$ and an $Na_2O \cdot 3V_2O_5$ complex. Free vanadium pentoxide itself, although quite corrosive, would be expected to exist only in Na_2SO_4 — V_2O_5 mixtures containing more than 88.8 percent V_2O_5. Na_2SO_4 and SO_3 are other potential corrosive compounds that could be present in oil ash.

Usually, only about 1 to 3 percent of the sulfur in oil is converted to SO_3 during combustion. Interest in the presence of SO_3 in combustion atmospheres has been concerned mainly with its corrosive effect at low temperatures (400 F) and with the problem of sulfate deposit formation on high-temperature surfaces. Cunningham and Brasunas[19] reported that the dissociation temperature of Na_2SO_4 is decreased markedly by the presence of V_2O_5. Reaction between Na_2SO_4 and V_2O_5 at temperatures above about 1400 F will form vanadates with

the evolution of SO_3 as a dissociation product. The contribution of SO_3 to the increase in pressure was clearly demonstrated in the pressure-temperature curves of Na_2SO_4 — V_2O_5 mixtures mentioned above. This was also discussed by Foster et al.[20] and a preliminary corrosion experiment in a prefused Na_2SO_4 — V_2O_5 mixture, compared with the same mixture which had not been prefused, demonstrated the strong corrosive effects of SO_3 evolved in the reaction. Any tendency for the evolved SO_3 to break down to SO_2 and O_2, according to equilibrium requirements, would make additional oxygen available for oxidation at the metal surfaces. This oxygen would probably be present in the nascent, highly reactive condition.

Thus, in these recent studies, evidence has been presented to substantiate the hypothesis that accelerated corrosion by vanadium-containing ash is initiated with the destruction of protective films by molten complex compounds and is continued by the reaction of the active metal surface with oxygen that is absorbed in the molten material. Pervious oxide films are formed which permit access of additional oxygen to the molten layer. In the above work, equilibrium conditions in simple mixtures have been assumed and it was granted that changes in operating conditions, the presence of other ash constituents and corrosion reactions with the metal could modify the indicated mechanism. The results are presented only as an approximation which could serve as a basis for further studies.

Cirilli, et al.[22,23,24] have started some similar basic work to establish equilibrium diagrams of V_2O_5 and various metal oxides, to help in the identification of compounds in the corrosion products of alloys attacked by V_2O_5. The existence of chromium, iron, nickel and cobalt vanadates was reported, but this was not correlated with their appearance in corrosion products of the alloys.

Sodium sulfate may be responsible for severe corrosion effects at temperatures considerably below its melting point. Shirley[25] reported that severe intergranular sulfur penetration and accelerated surface oxidation occurred at about 1300 F on certain alloys in contact with Na_2SO_4 contaminated with about 1 percent NaCl. The intergranular sulfidation on a high nickel alloy was much greater than that obtained on exposure to gaseous sulfur compounds. It was found that calcium sulfate in combination with sodium chloride had a similar effect on Type 18-8 stainless steel. Simons, Browning, and Liebhafsky[26] have studied the problem of Na_2SO_4 attack, referring to earlier reports of corrosion of alloy steels in contact with sodium sulfate contaminated with carbon. The reducing effect of carbon should provide the environment required for sulfur penetration into the steels. Results with pure Na_2SO_4 tend to be erratic, varying from no attack to complete destruction of the metal. These investigators suggested that a triggering mechanism consisting of a reducing effect is necessary to start the reaction after which it would proceed

rapidly. It was theorized that reduction to sulfate provides a lower-valent sulfur which reacts with the metal to form a low-melting sulfide, attacking the metal and penetrating into the grain boundaries. This is then followed by an autocatalytic oxidation reaction of the sulfide by Na_2SO_4 resulting in rapid oxidation of the metal. Experiments were made in which the triggering action was initiated by chemical and electrochemical means designed to produce reducing environments and these verified part of the proposed mechanism.

These studies point to the troubles that may be experienced from sodium and sulfur at gas-turbine temperatures even when using low-vanadium residual oils.

Evaluation of Materials of Construction

From a practical standpoint, a primary interest of users of residual fuels was naturally along the lines of finding materials of construction that would withstand the corrosive environment. Therefore, in many of the early investigations, the objective was to evaluate the high-temperature corrosion resistance of a variety of heat-resistant alloys, with the hope of either finding a useful material, or some promising indication that would lead to the development of a more resistant material. This became a formidable undertaking because of the many factors that had to be taken into consideration. The complex interactions of the products of combustion have already been noted. In addition, quantity of ash, metal surface temperature, gas temperature, time, velocity of combustion gases and thermal cycling are among the variables which could influence the corrosion results. Kind[27] has indicated that it is impossible to reproduce in the laboratory all of the conditions prevailing in a gas turbine. The ash-forming constituents can occur in the gaseous, liquid, or solid state and the different phases cannot be determined because the chemical and physical equilibria are changing continually. For this reason, simple laboratory tests have been condemned as being unrealistic, but Frederick and Eden,[28] among others, have found them to be almost indispensable guides to determine the course of more elaborate experiments. One simple test that has been used consists merely of placing a small quantity of ash, or ash component, on an alloy specimen and heating in air. A more elaborate test can be conducted in an experimental rig consisting of a combustion chamber, where gases are produced and a section where specimens are exposed to combustion products under conditions which exist in a gas turbine. Between these extremes, a variety of methods have been used to evaluate the behavior of materials or to investigate other factors related to the problem. Most of the methods fall in one of the following categories:

1. **Crucible Tests.** Specimens are wholly or partially immersed in actual or synthetic ash, and heated in air.

2. **Alternate Immersion Tests.** Specimens are alternately imersed in molten ash and exposed to hot oxidizing at-

mosphere. A modification of this procedure involves coating the test specimens with a thin slurry representative of the ash, at intervals to simulate continual ash deposition.

3. **Oxygen Consumption Method.** Specimens pre-coated with a layer of actual or synthetic ash are then exposed to oxygen in a hot furnace. The test measures the volume of oxygen consumed by the oxidizing surface.

4. **Furnace Tests.** Specimens in laboratory furnaces are exposed to flow of hot, synthetic or actual combustion products. Extension of this is a field test in which test specimens are suspended at desired locations in operating boilers.

5. **Gas Turbine Rig Tests** at atmospheric pressure and simulated operating conditions.

6. **Gas Turbine Rigs** operating at actual turbine pressures and gas flows.

It should be noted that some of these procedures should provide results of general value, whereas others are specific for either steam boilers or gas turbines.

Schläpfer, Amgwerd and Preis[15], Evans,[7] Buckland, Gardiner and Sanders[9] and Skinner and Kozlik[29] were among the early investigators who used the crucible test in exploratory work for screening of alloys and observing the effect of some variables. Their results cannot be compared quantitatively because of other differences in test procedures, but some of their general conclusions are in agreement, and have been verified by later work. For example, Skinner of Kozlik[29] reported that nickel base alloys were resistant to vanadium pentoxide, but were severely corroded in ash mixtures containing large percentages of sodium sulfate. Similarly, molybdenum-containing alloys were severely attacked in vanadium environments at high temperature. On the other hand, the chromium-iron alloys containing about 26 percent chromium such as AISI 446 performed better than other alloys under a variety of conditions. These comparisons are relative and both Evans[7] and Buckland, et al.[9] concluded that no alloy or class of materials which had been tested up to the time of their experiments could be considered to have a satisfactory service life for boilers and gas turbines burning residual fuels.

Nevertheless, the search for a useful material has continued and a number of additional papers have appeared describing the results of new work.[30-45] Many of these merely corroborated earlier results and provided corrosion data on additional alloys exposed to vanadium containing fuel ashes.

Oliver and Harris[34] and Harris, Child and Kerr[39] used a testing procedure which involved applying vanadium pentoxide on metal surfaces by painting them with a suspension of V_2O_5 in benzene and drying. This was followed by exposure to preheated air for 24 or 70 hours. Corrosion was evaluated by weight loss after descaling. Four and sixteen 70-hour cycles were used. A variety of gas-turbine alloys were tested and it was shown that a rapid increase in the rate of oxidation occurred at about

1400 F. The general effects of contamination with V_2O_5 was to lower markedly the useful service temperature of the alloys. Some alloys were comparatively better than others. G39, a 65 Ni — 20 Cr alloy containing W, Mo, Nb and Ta proved to be the most resistant in this test, being corroded at a rate of slightly less than 10 mg/sq cm/24 hr at 1750 F. These authors also studied the effect of various addition elements to the 20 Ni, 20 Co, 20 Cr, iron-base alloy. It was found that, of the additions tried, vanadium lowered the scaling resistance. Significantly, the addition of up to 10 percent Mo was not harmful to the resistance to V_2O_5 attack. This is in contrast to the reported deleterious effects of molybdenum in lower alloys.

Fitzer and Schwab[32] used a testing procedure which was designed to get results quickly. Specimens were scaled at about 1700F for 15-minute periods in a stream of oxygen, followed by brief immersions in molten V_2O_5 at 1650 F. This cyclic treatment could be continued as long as desired. The use of pure oxygen and 100 percent V_2O_5 were not thought to affect the mechanism of the corrosive reaction other than to accelerate it greatly. The beneficial effect of silicon as an alloying component was shown by this procedure in an experiment which extended over a relatively short period (2½ hours). Silicon was present in all of the best alloys. The most resistant material was Sicromal 12, a 23 percent chromium steel containing aluminum and about 3 percent silicon. Fitzer and Schwab attributed this to the good resistance of SiO_2 to attack by molten V_2O_5. In contrast, the chromium-containing scale layers formed on the austenitic chromium steels are said to be destroyed by V_2O_5. Reference was made to experiments still in progress which were designed to enrich the surface of useful alloys in silicon, thereby achieving better resistance to vanadium attack without sacrifice to the mechanical properties.

Alloy evaluation data obtained at the Naval Boiler and Turbine Laboratory were presented in reports by J. R. Witmeyer.[36, 37] Special alloys were immersed in synthetic high-sodium and high-vanadium mixtures at 1700, 2000 and 2200 F. An alloy of 60 Cr — 40 Fe displayed best corrosion resistance followed by 60 Cr — 40 Ni, 50 Cr — 50 Ni, Kanthal, and AISI 310. Although some of these alloys may not be fabricable into the desired form, the corrosion results show the experimental alloys to be superior to standard heat-resistant alloys. However, some investigators feel that accelerated corrosion is merely delayed under such circumstances and that the gain is not significant in the long life expectancy of boilers and gas turbines. Lucas, Weddle, and Preece[40] studied the oxidation of chromium at 1300 F in contact with V_2O_5, and concluded that an alloy depending on chromium for its oxidation resistance would not withstand V_2O_5 attack unless some means for preventing the diffusion of vanadium ions in the Cr_2O_3 film can be found. Some of the discussors of this paper[41] were not in

complete agreement with the above view indicating that, while no known chromium alloy is entirely satisfactory, some benefits have been derived with certain chromium alloys. The resistance of pure chromium to several synthetic ashes was investigated at the U. S. Naval Engineering Experiment Station.[42] The oxygen-consumption method was used in their experiments. Specimens are first contaminated by immersion in the molten ashes at 1600 F for two hours and then heated in a tube furnace at the desired temperature in an atmosphere of oxygen. The quantity of oxygen consumed was used as a measure of the extent of corrosion and indicated whether the contaminating ash accelerated the oxidation. It was reported that a very mild oxidation of chromium occurred under the slags containing vanadium. It was unaffected by a mixture of 90% Na_2SO_4 — 10%NaCl which caused catastrophic oxidation of alloys such as AISI 310. Stephenson,[41] in discussing the work at the National Gas Turbine Establishment, referred to some experiences with Ni-Be alloys which showed them to possess improved resistance to both vanadium and sodium ashes. This was attributed to the formation of a protective film of beryllia.

Betteridge, Sachs and Lewis[30] were concerned with the effect of ash attack on the high-temperature mechanical properties of materials of construction. Stress-rupture test bars were painted with water pastes of mixtures of V_2O_5 and Na_2SO_4 and then tested at about 1400 F. It was found that contamination with the mixtures shortened the life under stress of all materials. The decrease in stress-rupture life of Fe-base alloys was caused by a reduction in the cross-section of the test bar by uniform and progressive scaling. In Ni-base alloys, intergranular penetration led to scattered stress-rupture results. These observations indicate that the effective metal thickness determines the strength of the construction materials and that subsurface attack, which is not so readily detected, may result in serious weakening of the structural parts. In this connection, Sulzer and Bowen[43] referred to unpublished work in England, recommending a technique for the study of corrosion which evaluates the effect of intergranular attack. Tensile specimens are exposed to the products of combustion in a gas turbine, and withdrawn at intervals of about 500 hours. The change in tensile strength as a result of corrosion is determined and this is correlated with weight loss data and metallographic examination of cross-sections of the specimens for evidence of intergranular attack.

The corrosion behavior of selected heat-resistant alloys suspended in an operating steam boiler was described by McDowell, Raudebaugh and Somers.[31] The investigation was conducted at the Marion Generating Station of the Public Service Gas and Electric Company. Test racks were suspended from the high-temperature superheater tubes and presumably attained the gas temperature at that location. This varied from

1050 to 1560 F, depending on the boiler load. The boiler was fired with Bunker C oil. Exposure periods of three test racks varied from about 500 to 700 hours. The depth of attack was measured under a micrometer microscope. The alloys were rated comparatively from best to worst and Type 406 (12 Cr — 3 Al iron-base alloy) showed the least corrosion penetration, a fairly uniform metal loss of about 0.1-inch per year. It was thought Al_2O_3 formed from the aluminum in this alloy provided some protective effect. Corrosion of Inconel was also at a rate of about 0.1-inch per year, but in this case sulfidation and intergranular oxide penetration was observed. AISI 446, Incoloy and AISI 309 were next best in that order. For comparison, AISI 302 corroded at a rate of about 0.4-inch per year. The authors concluded that none of the alloys tested showed outstanding oxidation resistance and many of them certainly would be unsatisfactory for application in the high-temperature superheater sections of boilers.

The corrosion resistance of experimental alloys has been evaluated in recent work at the Naval Research Laboratories and the U.S. Naval Engineering Experiment Station.[46] In a microburner combustion rig, 100-hour tests at 1600 F showed that iron-chromium-aluminum alloys containing 25 percent Cr and 3.5 to 9.5 percent Al were corroded at much slower rates than AISI 310. Only slightly less resistant were 60 Cr — 40 Fe, 60 Cr — 40 Ni, and 50 Cr — 50 Ni alloys. The use of these alloys would extend the life of parts such as boiler tube supports in naval boilers using residual fuel oils. The use of vacuum melting procedures in the preparation of these alloys has resulted in improved workability and mechanical properties.

From these results, it does not appear that any of the available heat-resistant alloys can be recommended for use under all conditions of temperature and stress existing in the high-temperature zones of boilers and gas turbines burning residual oils. A few encouraging results have appeared in the data available on the behavior of experimental alloys. These merely indicate the avenues which might be explored in further work. The beneficial effects of chromium, aluminum, silicon and beryllium in alloys have been noted but the harmful effects of these elements on the metallurgical properties of alloys may limit their usefulness.

Protective Coatings

Relatively little information was found on the application and value of protective coatings against fuel oil ash. Dovey[47] merely lists surface coating methods which might be considered for this purpose. These included metal spraying, dipping, electroplating, vapor phase deposition, coating with ceramics and cladding with more resistant metals. No experimental results were given. Evans[7] tested a number of coatings on carbon and stainless steel specimens by partial immersion for 168 hours in a high-vanadium oil ash at 1350 F. Silicon impreg-

nation by a proprietary process provided the most protection for carbon steel, limiting the oxidation weight gain to that obtained by heating the steel in air. It was reported that the coating would not adhere to heat-resisting steels. Chromizing of carbon steel and AISI 430 was the next most promising treatment. Other coatings such as aluminizing, calorizing and galvanizing were partially protective. Srawley[48] tested aluminized AISI 310 steel by contaminating the surface with a mixture of equal parts of V_2O_5 and Na_2SO_4, and heating in a muffle furnace at 1700 F. In this test, aluminizing did not reduce corrosion to any significant extent, but it was indicated that a more extensive investigation should be made before making final conclusions. Frederick and Eden[28] examined the effect of V_2O_5 plus 10% Na_2SO_4 at 1240 F on nickel and chromium electrodeposits. Nickel offered little resistance to attack, having begun to disintegrate after 200 hours' exposure. On the other hand, the chromium electrodeposit was resistant itself, but failed by cracking due to the difference in thermal expansion between the coating and the basis metal. Lewis, in discussing Frederick and Eden's results, reported that a wide range of coating materials had been tested at the Thornton Research Center in England. In their experiments also, the coatings disintegrated either as a result of oxidation through pores in the coatings or as a result of differential expansion between the coating and the basis metal. Lewis thought that chromized layers would diffuse inwards upon prolonged exposure to elevated temperature. Therefore, he suggested better results might be obtained by chromizing alloys having some inherent oxidation resistance. Samuel and Hoar, in further discussion, pointed out that improved chromizing procedures now made it possible to produce thermal-shock-resistant layers on complex heat-resistant alloys. Therefore further consideration of such coatings for protection against oil-ash was suggested. The development of protective diffusion layers of nickel-aluminum by thermal treatment of aluminum-coated Nimonic 75 was suggested by Buckle.[49] Others have indicated that exposure of aluminum-coated materials to service temperatures for long periods of time may result in complete diffusion of the aluminum into the basis metal. Further studies appear to be needed to determine whether diffusion layers are protective. Several coated, heat-resistant casting alloys were included in the tests reported by McDowell.[31] The coatings were of the ceramic type, consisting of a mixture of oxides applied to the specimens and fired at a high temperature. After exposure of about 700 hours in the superheater zone of an oil-fired boiler, the coatings had chipped and cracked but had not been penetrated completely. Micrographic examination revealed a layer at the metal-coating interface which appeared to have resisted corrosive attack. This type of coating also was shown to be protective in one of the case histories included in the NACE Technical Committee Re-

port.[5] King and Nutt[13] in summarizing the work done for the U. S. Navy, referred to materials which are virtually unattacked by synthetic fuel ash mixtures at 1600 F. These include alumina, thoria, alumina-chromium cermets and nickel and chromium borides. Procedures for applying these materials to metal surfaces were not discussed.

Application of protective coatings by metal spraying was considered as a means for preventing the corrosion occurring in mercury boilers.[6] Sprayed layers of 26 percent Cr — Fe alloys were found to have good inherent resistance to oil-ash corrosion. This is in agreement with the good corrosion resistance of AISI 446 reported earlier. It was indicated however that the value of such coatings would depend on proper surface pretreatment and possibly a post treatment, to provide an impervious coating and a metallurgical bond at the metal-coating interface.

Thus, it appears that some relatively ash-resistant materials exist, but the problem of applying them to metal surfaces economically and in a useful form has not been solved. Further work on the development of protective surface coatings may be justified on the assumption that higher concentrations of beneficial elements can be tolerated in surface layers, rather than as alloying ingredients, without excessive harm to the physical properties of the alloy.

The Oil-Additive Approach

The oil-additive approach has appealed to almost everyone concerned with corrosion and fouling problems in oil-fired systems. On the basis of promising results obtained in early exploratory work, most investigators felt that a search for an inhibiting additive would, perhaps, be more fruitful than to search for a corrosion-resistant alloy. Furthermore, ash deposits also have been a source of trouble, causing blocking of gas passages in boilers and reduction in gas turbine efficiency. An additive that would cure both problems, obviously, would be highly desirable.

Because accelerated corrosion was associated with the presence of a molten ash on the metal surface, Evans[7] suggested that the function of a suitable additive should be to react chemically with the harmful ash components, forming compounds which would be solid at the operating temperature. According to the constitution diagram of the CaO — V_2O_5 system, the compound $3CaO \cdot V_2O_5$ has a melting point of about 2500 F, so this material was used in exploratory crucible tests to prove the point. Specimens immersed in $3CaO \cdot V_2O_5$, or in 1:1 (by weight) mixtures of CaO and a vanadium-containing oil ash at 1350 and 1500 F were unattacked after 168 hours' exposure. Evans also pointed out that if the weight of CaO used was less than 23.5 percent of the weight of V_2O_5, a eutectic melting at only 1150 F would form, thus making the ash more harmful by lowering, rather than raising, its melting point. Several other investigators[1,18,38,40,50] have obtained information on the effect of additives on the fusion

or softening point of oil ash and some of its constituents. The results are not directly comparable because different experimental techniques were used. There was general agreement that magnesium and calcium oxides were the most effective materials in raising the fusion point. Nickel oxide was also effective. Aluminum oxide was reported to have no effect on the melting of ash in concentrations up to 50 percent by weight of the ash. However, when used at higher concentrations, alumina caused a sharp increase in the melting point of a V_2O_5 — Al_2O_3 mixture. In several of the experiments,[18, 38] good correlation was obtained between ash-fusion temperatures and extent of corrosion. The work of Frederick and Eden,[28] however, indicates that at certain additive concentrations almost all materials could increase corrosion.

Many screening tests to evaluate possible additives have been conducted,[9, 11, 51, 52] using test procedures ranging from crucible tests to experiments in an industrial gas turbine. In line with their effect on ash melting point, calcium and magnesium compounds appear to be the most promising additives, although compounds of manganese, antimony, iron and the rare earths have been found to have inhibiting effects also. Selection of an additive is not determined solely by its corrosion-inhibiting effects. Some of the other requirements[5] include low cost, commercial availability, effectiveness over a range of temperatures and on various alloys in the system. Improved effectiveness may perhaps be obtained by using an oil-soluble additive which will have intimate contact with the oil droplets,[53] but this may add to the expense. E. B. Evans, et al.[11] have shown that under some conditions additives which reduce corrosion, also cause an increase in deposit formation. Also, it was reported that the order of effectiveness of the best materials is different on iron-base alloys from that on nickel-base alloys and may change with temperature.

Young and Hershey[54] calculated melting point curves for several binary systems of ash constituents and possible additives to determine which compounds should be effective additives from a theoretical standpoint. Certain simplifying assumptions were made in these calculations and, therefore, the conclusions were considered speculative. Taking into account melting point and stability, it was concluded that aluminum compounds should be desirable additives. Magnesium and calcium compounds were less desirable because of the high dissociation temperature of their sulfates. These conclusions should be verified under actual operating conditions, where the effect of any departure from the assumptions made in the calculation would be observed.

In a recent article, Jarvis[55] has summarized the experiences on the use of additives at several power plants in Europe and America. Dolomite (about 60 percent $CaCO_3$, 40 percent $MgCO_3$) was used in all of these plants, primarily to reduce the formation of bonded deposits in the superheater zone and low-temperature corrosion by the flue gases. It was reported that dolomite made the removal of deposits somewhat easier, but in some cases an increase in slagging in the combustion zone and superheater blockage was observed.

The treatment of residual oil and the use of additives in commercial gas turbines has been described in the publications of Buckland and his associates.[56, 57] The procedure which has been developed after several years of investigation includes a desalting treatment of the oil to reduce the sodium and calcium content. An aqueous magnesium sulfate wash solution is used, followed by centrifuging to reduce the sodium content of the oil to 10 ppm or less. The result is to reduce deposit formation during operation of the turbine to acceptable values. The effects of vanadium in the oil then can be minimized by magnesium sulfate added as a water solution to the oil prior to combustion. In a 2400-hour test run at 1450-1500 F with a fuel containing 360 ppm vanadium, Buckland reported that the corrosion of nozzles and buckets was not much greater than would occur when burning natural gas. The cost of such a treatment appears to be acceptable for gas-turbine operation, but it is not attractive to large utilities under present conditions.

Summary

Use of residual fuel oils in steam boilers and gas turbines operating at temperatures above 1100 F has focused attention on the important corrosion problems that arise under such conditions. There is ample evidence that corrosion is caused by the vanadium, sodium and sulfur that occur in the ash. Compounds of low melting point are formed during the course of the combustion reaction, or perhaps by reactions taking place following combustion. These compounds appear to have strong fluxing action when molten and in some manner act as oxygen carriers which result in accelerated corrosion at the metal-oxide interface. Economical procedures for removal of these elements have not been found.

Many testing procedures have been used to evaluate the behavior of heat-resistant alloys in these corrosive environments. While quantitative comparisons cannot be made, there appears to be general agreement that none of the presently-known alloys would have an acceptable service life under the conditions existing in boilers and gas turbines burning residual oils. Nevertheless, some alloys are more resistant than others and encouraging results have been obtained with some experimental alloys. Alloying additions such as silicon and aluminum are beneficial in this respect. The improved performance of experimental alloys indicates that the possibilities for a satisfactory solution to the problem may become more attractive as progress is made in the development of high-temperature alloys.

Experiences with protective coatings also have been discouraging. While certain coatings appeared to have fair inherent corrosion resistance, they have failed by cracking and undermining. Here also the possibility of obtaining improved coatings with beneficial elements concentrated in the outer surface layer of the metal is still open.

The study of oil additives has received the greatest amount of attention. The approach is straightforward and the objective has been to add materials to the oil which react with the harmful components to form compounds which are solid at operating temperatures. Calcium, magnesium, aluminum and silicon compounds are most effective. Additives appear to have specific effects, that is, they do not provide equal protective effects for all variations of impurities, operating conditions and materials of construction.

Progress has been reported in the studies of the basic mechanism of corrosion, in phase equilibrium relationships in systems comprising the harmful elements in residual oils and in thermochemical studies of additives. These should provide a better basis for future work and minimize the use of the empirical approach to the problem.

Acknowledgment

References

1. J. B. McIlroy, E. J. Holler, Jr. and R. B. Lee. The Application of Additives to Fuel Oil and Their Use in Steam Generating Units. *Trans. ASME,* 76, 31 (1954).
2. G. Weber. Heavy Fuel Oil. *The Oil and Gas J.,* 52, Pt. 6, 138 (1954).
3. J. F. Scott. Fuel-Oil Additives—Fact and Fiction. *Marine Eng.,* 62, No. 8, 75 (1957).
4. K. Sachs. Accelerated High Temperature Oxidation Due to Vanadium Pentoxide. *Metallurgia,* 57, 123 (1958); *Metallurgia,* 57, 167 (1958); *Metallurgia,* 57, 224 (1958).
5. NACE Technical Committee Report. The Present Status of the Oil Ash Corrosion Problem. *Corrosion,* 14, 369 t (1958).
6. A. M. Hall, D. Douglass and J. H. Jackson. Corrosion of Mercury-Boiler Tubes During Combustion of a Heavy Residual Oil. *Trans. ASME,* 75, 1037 (1953).
7. C. T. Evans. Oil Ash Corrosion of Materials at Elevated Temperatures. Symposium on Corrosion of Materials at Elevated Temperatures, STP, No. 8, ASTM, 59 (1951).
8. P. Draper. The Use of Residual Fuel Oils in Gas Turbines. ASME Paper No. 52-A-127 (1952).
9. B. O. Buckland, C. M. Gardiner and D. G. Sanders. Residual Fuel-Oil Ash Corrosion. ASME Paper No. 52-A-161 (1952).
10. H. Pfenninger, Experiences in Service With Gas Turbines Using Heavy Fuel Oils and the Application of Gas Turbines in the Petroleum Industry. Proc. Fourth World Petroleum Congress, Sect. VI/D, 263, (1955).
11. E. B. Evans, D. H. McLean, F. R. P. Sharp and A. Winward. The Use of Residual Fuels in Gas Turbines. Proc. Fourth World Petroleum Congress, Sect. VI/D, 291 (1955).
12. A. Lewis. Deposits From the Continuous Combustion of Oil Fuels. Proc. Fourth World Petroleum Congress, Sect. VI/D, 264 (1955).
13. H. F. King and H. V. Nutt. Fuels for U. S. Navy Gas Turbines. *Trans. ASME,* 78, 185 (1956).
14. G. Lucas and A. Pollock. Gas Turbine Materials, Temple Press Ltd., London, E.C. 1, 53 (1957).
15. P. Schlapfer, P. Amgwerd and H. Preis. Investigation of the Attack of Vanadium-Containing Fuel Oil Ashes Upon Heat-Resisting Steels. *Schweizer Archiv fur Angewandte Wissenschaft und Technik,* 15, 291 (1949).

16. J. L. Meijering and G. W. Rathenau. The Oxidation of Heat-Resistant Alloys in the Presence of Foreign Oxides. *Philips Technical Review*, 12, 213 (1951).
17. A. de S. Brasunas and N. J. Grant. Accelerated Oxidation of Metals at High Temperatures. *Trans. ASM*, 44, 1117 (1952).
18. F. C. Monkman and N. J. Grant. An Investigation of Accelerated Oxidation of Heat Resistant Metals due to Vanadium. *Corrosion*, 9, 460 (1953).
19. G. W. Cunningham and A. de S. Brasunas. The Effects of Contamination by Vanadium and Sodium Compounds in the Air Corrosion of Stainless Steels. *Corrosion*, 12, 389 t (1956).
20. W. R. Foster, M. H. Leipold and T. S. Shevlin. A Simple Phase Equilibrium Approach to the Problem of Oil Ash Corrosion. *Corrosion*, 12, 539 t (1956).
21. C. C. Hale and P. K. Starnes. The Use of Physical Methods in Determining the Cause of Corrosion by Fuel Ash. Unpublished manuscript.
22. V. Cirilli, A. Burdese and C. Brisi. High Temperature Corrosion of Metals by Vanadium Pentoxide—Part I. Research on the System Metal-Vanadium-Oxygen. *Metallurgia Italiana*, 48, 309 (1956).
23. A. Burdese and C. Brisi. High Temperature Corrosion of Metals by Vanadium Pentoxide—Part II. Behavior of Some Metals (Iron, Cobalt, Nickel, and Chromium) and Their Alloys. *Metallurgia Italiana*, 48, 349 (1956).
24. V. Cirilli and A. Burdese. Corrosive Action of Vanadium Pentoxide on Metals. *Metallurgia Italiana*, 49, 320 (1957).
25. H. T. Shirley. Effect of Sulfate-Chloride Mixtures in Fuel Ash Corrosion of Steels and High Nickel Alloys. *JISI*, 182, 144 (1956).
26. E. L. Simons, G. V. Browning and H. A. Liebhafsky. Sodium Sulfate in Gas Turbines. *Corrosion*, 11, 505 t (1955).
27. C. Kind. Experimental Set-Up for Investigating Ash Deposition and Corrosion Phenomena on Gas-Turbine Materials at High Temperatures. *Brown Boveri Review*, 40, 196 (April, 1953).
28. S. H. Frederick and T. F. Eden. Corrosion Aspects of the Vanadium Problem in Gas Turbines. *Corrosion*, 11, 19 t (1955).
29. E. N. Skinner and R. A. Kozlik. Corrosion of Alloys at High Temperatures with Special Reference to Attack by Vanadium Pentoxide. Unpublished manuscript.
30. W. Betteridge, K. Sachs and H. Lewis. The Influence of Vanadium Pentoxide on the High Temperature Scaling of Heat Resisting Alloys. *J. Inst. Petroleum*, 41, 170 (1955).
31. D. W. McDowell, R. J. Raudebaugh and W. E. Somers. High Temperature Corrosion of Alloys Exposed in the Superheater of an Oil-Fired Boiler. *Trans. ASME*, 79, 319 (1957).
32. E. Fitzer and J. Schwab. Attack of Scaling-Resistant Materials by Vanadium Pentoxide and Effect of Various Alloying Elements Thereon. *Corrosion*, 12, 459 t (1956).
33. F. Gallman, J. Friedli and W. Epprecht. Surface Corrosion of Heat-Resisting Materials Under the Action of Bunker Oil Ashes Containing Sodium, Sulfur, and Vanadium. Proc. Third World Petroleum Congress, Sect. VIII, 32 (1951).
34. D. A. Oliver and G. T. Harris. Some Proven Gas Turbine Steels and Related Developments. Symposium on High-Temperature Steels and Alloys for Gas Turbines. Special Report No. 43, The Iron and Steel Institute, London, 51 (1952).
35. C. Sykes and H. T. Shirley. Scaling of Heat Resisting Steels: Influence of Combustible Sulfur and Oil-Fuel Ash Constituents. Symposium on High-Temperature Steels and Alloys for Gas Turbines. Special Report No. 43, The Iron and Steel Institute, London, 153 (1952).
36. J. R. Witmeyer. Fuel Oil Ash Corrosion Resistance of 'Kanthal' Alloy. NBTL Test Report No. R-253, AD-143765 (June 26, 1957).
37. J. R. Witmeyer. Fuel Oil Ash Corrosion Resistance of Chromium Metal. NBTL Test Report No. R-255, AD-147471 (July 27, 1957).
38. W. E. Young, A. E. Hershey and C. E. Hussey. The Evaluation of Corrosion Resistance for Gas Turbine Blade Materials. *Trans. ASME*, 77, 985 (1955).
39. G. T. Harris, H. C. Child and J. A. Kerr. Effect of the Composition of Gas-Turbine Alloys on Resistance to Scaling and to Vanadium Pentoxide Attack. *JISI*, 179, 241 (1955).
40. G. Lucas, M. Weddle and A. Preece. The Liquidus of Metal Oxide/V2O5 Systems and the Mechanism of Accelerated Attack on Metals by V2O5. *JISI*, 179, 342 (1955).
41. Discussion on References 39 and 40. *JISI*, 182, 195 (1956).
42. U. S. Naval Engineering Experiment Station, Unpublished Report No. 040088E (May 7, 1957).
43. R. P. Sulzer and I. G. Bowen. Combustion of Residual Fuels in Gas Turbines. Proceedings of the Joint Conference on Combustion, The Institution of Mechanical Engineers, London, 386-389 (1955).
44. J. J. MacFarlane and F. S. E. Whitcher. The Fouling of Turbine Blades by Fuel Ash. Part IV. Pressure Tests with Cambered Blades. NGTE Report No. R-193 (July, 1956).
45. F. S. E. Whitcher. The Fouling of Turbine Blades by Fuel Ash. Part V. Corrosion Tests with Various Heat Resisting Materials. NGTE Report No. R-192 (June, 1956).
46. J. E. Srawley. Iron-Chromium-Aluminum Alloys. NRL Report 5124 (1958).
47. D. M. Dovey. Protective Coatings on Metals. Increasing Life at High Temperatures. *Metal Treatment and Drop Forging*, 20, 341 (1953).
48. J. E. Srawley. Fuel Ash Attack on Aluminum-Coated Stainless Steel. *Corrosion*, 14, 56 t (1958).
49. H. Buckle. Protection Against Oxidation of High-Temperature Alloys Using Multi-Phase Diffusion Processes. *Rev. Met.*, 54, 16 (1957).
50. R. S. Norris. A Liquid Additive to Limit Oil Ash Corrosion. *Corrosion*, 13, 123 (1957).
51. U. S. Naval Engineering Experiment Station, Unpublished Report No. 070034C (April 17, 1957).
52. R. C. Amero, A. G. Rocchini and C. E. Trautman. Small-Scale Burner Tests to Investigate Oil-Ash Corrosion. ASME Paper No. 58-GTP-19 (March, 1958).
53. Peter T. Sulzer. The Prevention of Oil-Ash Deposition by Means of Fuel Additives. Proc. Fourth World Petroleum Congress, Section VI/D, 223 (1955).
54. W. E. Young and A. E. Hershey. A Thermochemical Study of Some Additives to Reduce Residual Fuel Ash Corrosion. *Corrosion*, 13, 725 t (1957).
55. W. D. Jarvis. The Selection and Use of Additives in Oil-Fired Boilers. *J. Inst. of Fuel*, 31, 480 (1958).
56. B. O. Buckland and D. G. Sanders. Modified Residual Fuel for Gas Turbines. *Trans. ASME*, 77, 1199 (1955).
57. B. O. Buckland. The Effect of Treated High-Vanadium Fuel on Gas Turbine Load, Efficiency and Life. ASME Paper No. 58-GTP-17 (1958).

Bibliography

W. Stauffer. Some Problems of High-Temperature Strength Heat-Resisting Steels as Studied From the User's Viewpoint. *Schweizer Archiv.*, 17, 353 (1951). H. Brutcher Translation No. 2903.

E. C. Huge. Better Burning, Less Corrosion From Residual Fuel Oil. Oil and Gas J., 53, Pt. 2, 90 (July 19, 1954).

Burnham W. King and Leon L. Suber. Some Properties of the Oxides of Vanadium and Their Compounds. *J. Am. Ceram. Soc.*, 38, No. 9, 306 (1955).

T. Widell and I. Juharaz. Softening Point of Residual Fuel Oil Ash. *Combustion*, 22, 51 (1951).

K. Konopicky. Technical Problems Concerning V2O5. *Brennstoff-Chemie*, 36, 151 (1955).

O. F. Campbell. Additives in Residual Fuels Reduce Ash Deposits on Steam Boiler Parts. Oil and Gas J., 52, Pt 6, 171 (March 22, 1954).

D. M. Landis. Washing System Cleans Up Residual Fuel for Low-Cost Gas Turbine Operation. *Power*, 99, 78 (1955).

J. Lamb and L. Birts. The 'Auris' Gas Turbine Project. ASME Paper No. 58-GTP-12 (1958).

P. T. Sulzer. The Influence of Some Chemical and Physical Factors on the Formation of Deposits From Residual Fuels. *Trans. ASME*, 77, 995 (1955).

J. B. Bucher. Gas Turbine Performance and Materials. Symposium on High-Temperature Steels and Alloys for Gas Turbines, Special Report No. 43, The Iron and Steel Institute, London, 17 (1952).

A. de S. Brasunas. Catastrophic Corrosion Resulting From Vanadium Pentoxide in Fuel Oil Ash. *Corrosion*, 11, 17 (1955).

J. T. Collins and W. T. Knox. A New Look at Heavy Fuel Oils. *Proc. Am. Petroleum Inst.*, 35 (III), 431 (1955).

O. Rosahl. Experiences with Combustion of Heavy Fuel Oil in Boiler Plant. *Mitt. Ver. Grosskesselbesitz*, 46, 13 (1957).

P. Lloyd and R. P. Probert. The Problem of Burning Residual Oils in Gas Turbines. *Proc. Inst. Mech. Engrs.*, 163, 206 (1950).

B. Engel. On Erosion and Corrosion Damage Caused by the Use of Heavy Fuel Oil in Engines, Boilers and Gas Turbines. *Erdol und Kohle*, 3, 321 (1950). H. Brutcher Translation No. 2656.

F. E. Clarke. Vanadium Ash Problems in Oil-Fired Boilers. *J. Am. Soc. Naval Engineers*, 65, 253 (1953).

H. L. Logan and W. Ambs. Corrosion of Stainless Steel in Fuel Oil Ash Contaminants. Nat. Bur. Stds. Report 4858 (September 30, 1956).

Any discussion of this article not published above will appear in the June, 1960 issue

l. 15

Ther-
Re-
sion,

Addi-
Fuel,

lified
ME,

High-
Effi-
P-17

era-
died
2903.
sion
Pt.

ome
heir
306

t of
51).
ning

uels
rts.
54).
Up
era-

Tur-
58).
ical
De-
995

and
eels
No.
17

Re-
Ash.

ook
st.,

ook
oss-

of

age
es,
3,

Oil-
65,

in-
at.

Electrical Resistance Method
for
Studying Corrosion Inhibitors
in
Automotive Anti-Freezes*

By J. C. CESSNA

Figure 1—Corrosion test assembly.

About

the

Author

J. C. CESSNA has been associated with the National Carbon Research Laboratories since 1952. He is engaged in corrosion studies and problems relating to anti-freezes. A graduate of Augustana College, and of Iowa State College with an MS in chemistry, he is a member of ACS, ECS, and NACE.

Introduction

THE ELECTRICAL resistance method for measuring the extent of corrosion is based on the fact that the resistance of a metal is inversely proportional to its cross-sectional area. The cross-sectional area of a metal decreases in a corrosive medium as corrosion proceeds and the resistance of the metal increases. Determination of the resistance of a metal specimen before, during and after the corrosion process indicates the extent of corrosion.

The electrical resistance method has been employed to study metal oxidation[1,2,3] and corrosion rates.[4,5] Recent publications have indicated more widespread interest in numerous applications.[6,7,8,9,10,11,12,13] The advantages of the method are: (1) determination of low corrosion rates; (2) determination of corrosion rates at any given time without disturbing the specimen; (3) continuous measurement of the corrosion rate is possible; and (4) changes in the corrosivity of the environment are rapidly detected. Measurements are simple to determine, rapid and require little elaborate apparatus. The disadvantages of the method include: (1) possible polarization effects; (2) conducting corrosion products; and (3) nonuniform corrosion. The use of alternating current or an interrupted small direct current, respectively, should eliminate or minimize polarization effects. No difference in metal corrosion rates has been detected between the interrupted direct current technique (30 seconds each 15 minutes) and intervals of 50 hours between readings. Although conducting corrosion products, such as sulfides, have been reported, no evidence of conducting products has been found under the testing conditions employed in the author's laboratories. Terrell and Lewis[8] observed that any error due to conducting films could be determined by comparing the resistance of the corroded specimen before and after removal of the corrosion products by chemical cleaning, making appropriate corrections for metal loss during the cleaning operation.

Nonuniform corrosion can produce erroneous results. Isolated localized corrosion forming pits and perforations produces erroneously high corrosion rates.

★ Submitted for publication December 11, 1958.

Abstract

The electrical resistance method has been employed to evaluate corrosion and corrosion inhibition in ethylene glycol-water solutions. Corrosion decreases the cross section of a metallic specimen with a subsequent increase in resistance. The extent of corrosion can then be determined from the change in resistance. The corrosion of iron, aluminum and cuprous metals is reported under varying test conditions of temperature, glycol concentrations and synthetic waters. The effect of some corrosion inhibitors upon these metals is illustrated.

Reasonably good correlation has been observed of the extent of corrosion measured by both resistance changes and by actual specimen weight loss. Pitting type of attack has been observed on many of the specimens; however, this attack has been uniformly distributed over the entire length of the specimen in practically all instances and has not prevented accurate determinations of corrosion rates. The concept of the use of precorroded metal surfaces in evaluating corrosion inhibitors has been enlarged upon. It has been observed that few corrosion inhibitors can stop effectively corrosion of a severely corroded metal specimen, whereas many corrosion inhibitors can maintain effectively the condition of an air-oxidized clean metal surface.   2.3.5

Visual inspection of the corroded specimen, together with weight loss measurements, can detect isolated localized attack of this kind easily. Tests employed in the author's laboratories have shown reasonably good correlation between the extent of corrosion determined by both the resistance method and weight loss measurements. Notable exception are discussed in detail in the appropriate sections.

This article discusses the application of the resistance technique to the determination of relative corrosion inhibitor effectiveness in the aqueous ethylene glycol system. Corrosion in the multimetal engine cooling system is a complex process influenced by a large number of factors. A number of these factors have been listed recently.[14] Changes in one or more of these variables frequently can determine whether or not a given corrosion inhibitor will provide adequate metal protection. Laboratory corrosion tests provide comparative results. Under a given set of testing conditions, relative corrosion rates and relative corrosion inhibitor effectiveness can be determined. Varying the testing conditions provides additional valuable information on the corrosion and corrosion inhibition process. However, until laboratory operating conditions are identical to those of the engine, caution must be observed in extrapolating laboratory results into field operations. Test conditions employed to determine relative inhibitor effectiveness are not those of an actual operating engine; thus, it is not intended that test results be directly applied to field use.

Experimental Procedures

Specimens

The typical dimensions of the specimens were 0.001 x 0.125 x 8.0-inches. These specimens were cut on a hand-operated shearing press from shim stock or foil. The steel and cuprous metals were degreased in benzene and then in hot dilute sodium hydroxide. A brief immersion in dilute hydrochloric acid was

followed by rinsing and drying with acetone. Aluminum samples were degreased by immersion in benzene, followed by a 30-second immersion in 1N sodium hydroxide with subsequent rinsing and drying with acetone. These specimens were weighed when required and attached to the lead wires. The "potential" and "current" leads were 4-inch copper wire (B and S gauge No. 24) soldered at each end of the specimen.

A typical molded specimen is shown in Figure 1. The molded specimen is fabricated in such a way that the soldered connection and lead wires are not exposed to the solution under test. This feature eliminates errors due to galvanic effects of the solder junction and to corrosion of the lead wires. The soldered junctions are cast in epoxy resin (three parts of resin ERL-2774 and one part of hardener ERL-2793). The average exposed metal specimen length after casting was 5.5 inches. The specimens were stored in a desiccator.

Metals

Composition and thickness of the metals employed in this report are given in Table 1. The metals were used as received.

Measuring Circuit

The method employed consisted of passing a small direct current through the specimen and measuring the potential drop across the leads. A block diagram of this circuit is illustrated in Figure 2. The d.c. source consisted of three 6-volt batteries connected in parallel. Leads across a fixed resistance of 0.5 ohm were employed to determine the current at any time. The relay timer was set so that the current was passed through the circuit for 30 seconds each 15 minutes in order to minimize polarization effects. The current employed varied from 15 milliamperes to 30 milliamperes depending upon the metal involved. The recording potentiometer had a 0-20 millivolt range.

Test Procedure

The molded specimens were removed from the desiccator, degreased with acetone and briefly immersed in a cleaning solution, rinsed and dried. Initial cleaning procedure on the molded specimens varied with the metal under consideration. The steel and cuprous metals were cleaned by a brief immersion in 1:1 hydrochloric acid and the aluminum by a 30 second immersion in 1N sodium hydroxide. The specimens were then inserted in a No. 14 rubber stopper. The assembly was then totally immersed in a 600 ml capacity tall-form beaker containing 460 ml of test solution. The test solution, unless otherwise specified, consisted of 33 percent (volume) ethylene glycol (iron and chloride free) in distilled water. The initial and continuing temperature was 77 C unless otherwise noted. Maximum temperature deviation was ±1.0 C. Because metals exhibit temperature coefficients of resistance, any temperature deviation from 77.0 C required that the data be corrected using experimentally determined corrections.

The heat source was a whirl bath containing a lubricant fluid. Aeration of 0.028 cfm was immediately applied and the initial resistance was obtained approximately two minutes after immersion of the test specimen. A water-cooled condenser was attached to the rubber stopper to minimize solution loss.

Calculations

The resistance technique is based on the fact that the resistance of a fixed length of metal is inversely proportional to the cross-sectional area. During the corrosion process, the cross section of the metal decreases and the resistance increases. The percentage loss of cross-sectional area is measured quantitatively by comparing the electrical resistance of the specimen at any given time with the initial resistance. The ratio of the cross section of the corroded strip to the original cross section is R_o/R, where R_o is the original resistance and R is the resistance at any given time. Corrosion loss relative to the original cross section can be expressed[8] as

$$\% \text{ Corrosion} = 100\left(1 - \frac{R_o}{R}\right) \quad (1)$$

The measured resistances, R_o and R, are corrected because part of the metal specimen is covered with epoxy resin and remains constant throughout the test. The length of this unexposed portion can be calculated by measuring the length of the specimen before and after the molding operation. The resistance of the unexposed portion is equal to the percent length of the unexposed portion times the measured initial resistance, since resistance is directly proportional to length. Therefore, the extent of corrosion under these conditions can be expressed as

$$\% \text{ Corrosion} = 100\left[1 - \left(\frac{R_o - R_u}{R - R_u}\right)\right] \quad (2)$$

where R_o is the initial measured resist-

ance, R is the measured resistance at any given time, and R_u is the (fixed) resistance of the unexposed portion of the metal specimen.

Weight losses of metal specimens have long been employed as a criterion for measuring the extent of corrosion. A check of the resistance technique results can be made by comparing these results to the weight losses of the actual specimens involved. The equation used to determine the extent of corrosion by weight loss measurements can be expressed as

$$\% \text{ Corrosion} = 100\left[\frac{(W_1 - x) - (W_2 + y)}{W_1 - x}\right] \quad (3)$$

where the initial and final weight of the metal specimens is represented, respectively, by W_1 and W_2, both expressed in milligrams per linear inch. The values x and y represent, respectively, the constant correction factor for the metal losses during the initial and final cleaning procedures, both expressed in milligrams per linear inch.

Experimental Results

Mild Steel

Uninhibited Ethylene Glycol Solutions. The standard test solution consisted of 33 percent (volume) ethylene glycol in distilled water. The average corrosion rate of mild steel in seven separate experiments is shown by Curve 1 in Figure 3. The corrosion rate was reasonably uniform during the test. The type of surface treatment had no significant effect on the initial corrosion rate under these conditions. The corrosion rates of specimens which were grit-blasted (Al_2O_3), or ground on a small grinding wheel (240 grit) were similar to those in Figure 3 which were chemically cleaned. The grinding and grit-blasting techniques usually produce more uniform surfaces and the subsequent corrosion rates are more reproducible; however, it is difficult to obtain accurate blanks because of the metal lost

Figure 2—Block diagram of DC electrical resistance corrosion apparatus.
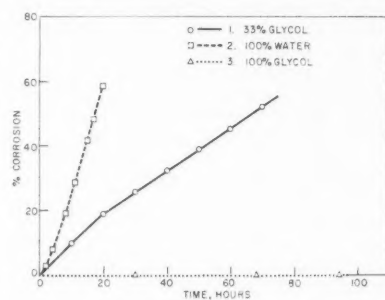
Figure 3—Corrosion of steel in ethylene glycol and water.

TABLE 1—Composition of Metals

No.	Metal	Thickness Mils	Percent Composition							
			C	Mn	P	S	Cu	Zn	Si	Fe
1	Mild Steel	1	.09	.31	.009	.029	.....	.....	....	....
2	Mild Steel	2	.10	.32	.002	.016	.....	.....	....	....
3	Aluminum	1	.01				.07	.....	.08	.58
4	Brass	1	....	....	....	....	69.51	30.45	....	....
5	Copper	1.4	....	....	....	....	99.63	.....	....	....
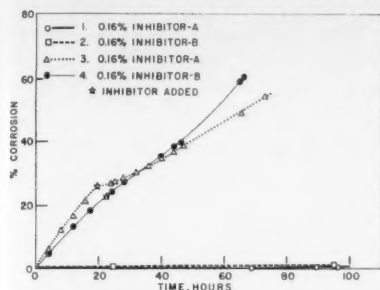
Figure 4—Corrosion of steel in glycol-water solutions with commercial corrosion inhibitors.
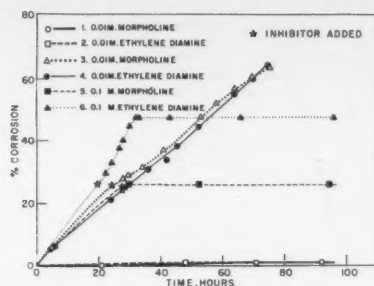
Figure 5—Corrosion of steel in glycol-water solutions with amine corrosion inhibitors.
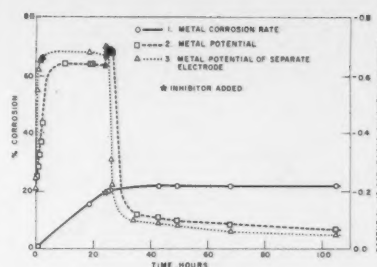
Figure 6—The corrosion rate and metal potential of steel in glycol-water solution with a polar-type oil.

during these cleaning operations. Once the resistance technique has been established as useful in a given environment, then weight loss measurements can be eliminated and specimens may be ground or grit-blasted for better reproducibility.

The initial corrosion rate of mild steel under these conditions of temperature and aeration is dependent upon the glycol concentration. Results obtained by varying the glycol concentration in the glycol-water system are illustrated in Figure 3. the high initial corrosion rate of mild steel in distilled water shown by Curve 2 in Figure 3 diminished when a 33 percent glycol solution was used, as shown by Curve 1. Essentially no corrosion was detected in a 100 percent ethylene glycol solution, as shown by Curve 3. It is interesting to note that the initial steel corrosion which occurred under these testing conditions is due to the presence of water. Each curve represents the average value of a minimum of two experiments. An identical series of experiments was made employing specimens of different dimensions (0.005 x 0.062 x 8.0-inches) with similar trends resulting. Tests of longer duration can be employed by use of specimens of larger cross section.

Reasonably uniform corrosion of mild

steel occurs in the uninhibited glycol-water system under the conditions of this corrosion test. Random distribution of the pitting and perforation type of attack is found as corrosion proceeds. This reasonably uniform distribution of metal attack is illustrated by Table 2. The individual tests illustrated in Table 2 were used to prepare the curves in Figure 3. Metal corrosion rates in the uninhibited glycol-water test solutions show that the percent corrosion values determined by actual weight losses are somewhat lower than those determined by resistance measurements. This observed discrepancy indicates that the metal attack is not completely uniform and appears to increase as the extent of corrosion increases.

Previous work[15] on atmospheric corrosion showed a direct relationship between resistance changes and calculated weight losses; however, the resistance changes indicated a much greater degree of corrosion. Denman's[10] work indicated a good relationship between the extent of corrosion measured by resistance values and the quantity of isolated corrosion products.

Inhibited Ethylene Glycol Solutions. The metal surface ordinarily employed in laboratory beaker corrosion tests is the clean air-oxidized (passive) metal surface. The advantages of such surfaces include easy determination of weight losses and visual observation of the type of attack. A relatively large number of corrosion inhibitors can maintain this rather inert initial surface, and subsequent protection results. Curves 1 and 2 in Figure 4 show that several commercial corrosion inhibitors advertised for use in glycol-water systems provide adequate protection to clean surfaces. The test solutions were 33 percent ethylene glycol in distilled water held at 77 C with constant aeration. The inhibitor concentration was 0.16 percent by volume (corresponding to 0.5 percent based on the glycol present). Curves 3 and 4 represent the action of these inhibitors under the same testing conditions, except that the steel surfaces were permitted to corrode before addition of the inhibitors. These inhibitors were not sufficiently effective to stop corrosion of an actively corroding steel surface. The corrosion rate was only slightly decreased. Further experiments not illustrated showed that doubling the inhibitor concentration did not stop corrosion. It is more difficult to stop corrosion on an actively corroding surface than to maintain initial passivity.

Figure 5 is included to show that this phenomenon is a general one and can be illustrated by inhibitors of known structure. Curves 1 and 2 illustrate, respectively, the corrosion rate of mild steel in the presence of 0.01 M (molar) morpholine (approximately 0.08 percent by weight based on total solution) and ethylene diamine (approximately 0.06 percent by weight based on total solution). These inhibitors adequately maintain the condition of a clean air-oxidized metal surface. Addition of the same concentration of morpholine and ethylene diamine to the actively corroding steel specimens is illustrated, respectively, by Curves 3 and 4. Corrosion was not stopped in these cases. Addition of 0.1 M morpholine (aproximately 0.83 percent by weight based on total solution) to the corroding media stopped corrosion as shown by Curve 5. Addition of 0.1 M ethylene diamine (approximately 0.57 percent by weight based on total solution) also stopped steel corrosion as illustrated by Curve 6. The inhibitors and concentrations shown in Figures 4 and 5 were selected solely to illustrate the differences observed in inhibiting corrosion of passive and active metal surfaces.

The action of a polar-type oil of known composition upon a precorroded metal surface is illustrated in Figure 6. The oil was prepared by adding 10 percent by weight of sodium dinonylnaphthalene sulfonate to a medium light mineral oil. This oil is referred to in subsequent experiments as the polar-type oil. The additive was obtained as a 50 percent dispersion. Curve 1 shows that the corrosion was essentially stopped by the addition of 0.29 percent (by weight, based on the total solution) of the oil to the corroded active metal surface. Curve 2 represents the potential-time behavior of the actual shim stock specimen. Addition of the oil produced a rapid shift in potential toward the passive direction. The action of the oil under these conditions is further shown by Curve 3 which is the potential-time behavior of a separate SAE 1030 mild steel electrode. The electrode surface was abraded on a 150-grit surfacer to hold water (as a test for a clean surface) and rubbed with wet, then dry, filter paper. The fabrication and use of such an electrode has been described elsewhere.[16] The metal potential again shifted toward the passive range. The combination of potential, resistance and weight loss measurements shows that corrosion has stopped.

TABLE 2—Relation Between Resistance Measurements and Weight Losses

Test* No.	Percent Glycol	Percent Corrosion	
		Resistance Changes	Weight Loss
1	0	64.5	52.0
2	0	59.7	52.2
3	0	57.8	52.8
4	33	62.7	58.0
5	33	77.5	71.3
6	33	23.5	22.1
7	33	23.1	21.3
8	33	45.9	35.9
9	33	49.8	38.9
10	100	0	0.9
11	100	0	1.1

* Each test was terminated at different times.

TABLE 3—Relation Between Resistance Measurements and Weight Losses

Figure	Curve	Test Duration Hours	Percent Corrosion	
			Resistance Changes	Weight Loss
6	1	105	22.2	20.9
7	1	76	57.6	42.1
	2	71	67.3	61.2
	3	94	29.5	26.9
	4	96	29.0	29.7
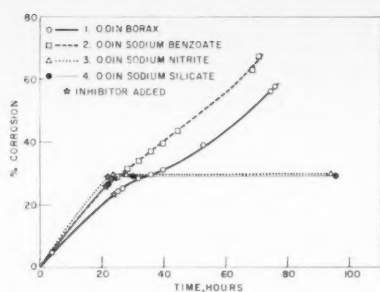
Figure 7—Corrosion of steel in glycol-water solutions with corrosion inhibitors.

Figure 8—Corrosion of steel in glycol-"corrosive" water solutions with corrosion inhibitors.

Figure 9—Corrosion of steel in glycol-"corrosive" water solutions with corrosion inhibitors.

Figure 10—Corrosion of steel in glycol-"corrosive" water solutions under cycling conditions.

The relation between resistance values and weight loss measurements for experiments illustrated in Figures 6 and 7 is shown in Table 3.

The difficulty of inhibiting corrosion of a ferrous metal surface increases as corrosion proceeds. It was shown that greater concentrations of inhibitors are required to establish inhibition of an active corroding surface than are required to maintain an initially clean air-oxidized surface. The clean air-oxidized surface represents an extreme of mild testing conditions, whereas the active precorroded surface represents an extreme of severe conditions. The condition of the metal surfaces found in automobile cooling systems is believed to be represented as an area between these extreme types. The surface condition of the cooling system, when an anti-freeze is added, is certainly not represented by the clean, relatively inert, surface condition of metals ordinarily employed in beaker corrosion tests. It further appears unlikely that the metals in the cooling system are continually corroding at the rates shown in Figure 3. The precorroded surface can be employed to advantage as a severe screening test to determine relative corrosion inhibitor effectiveness. The use of the precorroded metal surface in evaluating corrosion inhibitors has been employed in the author's laboratories for several years and is considered a valuable screening tool. The use of metal surfaces in various degrees of corrosion has been reported by various investigators.[10, 12, 13]

The relative effectiveness of a number of corrosion inhibitors upon precorroded mild steel surfaces is shown in Figure 7. Sufficient inhibitor was added to the glycol-water solution to produce a concentration of 0.01N after a precorrosion duration of approximately 24 hours at the indicated points. Addition of sufficient borax to produce a 0.01 N solution (approximately 0.18 percent by weight of $Na_2B_4O_7 \cdot 10H_2O$ based on total solution) did not provide adequate metal protection, as shown by Curve 1. Sodium benzoate at 0.01N concentration (approximately 0.14 percent by weight of C_6H_5COONa based on total solution) did not stop corrosion under these conditions (Curve 2). Sodium nitrite (approximately 0.07 percent by weight of $NaNO_2$) and sodium metasilicate (approximately 0.14 percent by weight of $Na_2SiO_3 \cdot 9H_2O$) provided adequate metal protection as shown respectively by Curves 3 and 4.
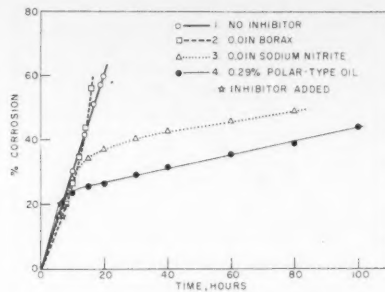
Synthetic "corrosive" waters are frequently employed to differentiate among corrosion inhibitors. A specific corrosive water was adapted containing 100 ppm each of chloride, sulfate and bicarbonate ions, all as the sodium salt. This concentration and type of corrosive water was selected solely to increase the metal corrosion rate, and to examine inhibitor action in the presence of the "corrosive" anions. The corrosion rate of mild steel in ethylene glycol diluted to 33 percent with this specific corrosive water is illustrated by Curve 1 in Figure 8. The corrosion inhibitors were added to the corrosive media at approximately seven hours after the test started. As shown by Curve 2, borax (0.01N) was ineffective in stopping corrosion under these severe conditions. The action of the polar-type oil (0.29 percent by weight based on total solution) produced best protection (Curve 4), but was not adequate under these severe testing conditions. Sodium nitrite (0.01N) was somewhat effective, but did not stop corrosion (Curve 3).

The combination of precorroded surface and corrosive water constitutes a severe corrosion test. A milder test can be employed using an initially air-oxidized mild steel surface and ethylene glycol diluted to 33 percent with the corrosive water. Figure 9 illustrates the corrosion pattern of mild steel when both the inhibitor and glycol-corrosive water are present in the solution before introduction of the metal specimen. Curve 1 again shows the rapid corrosion rate in the uninhibited solution. Curve 2 illustrates the ineffective inhibiting action of borax (0.01N) under these milder conditions. Curve 3 represents the adequate protection afforded by sodium nitrite (0.01N). The polar-type oil (0.29 percent by weight) previously described provided adequate protection (Curve 4) under these conditions.

The effects of temperature and aeration cycling are graphically represented by use of the resistance technique. The results of such cycling are shown in Figure 10. Specimens of greater cross-sectional areas (0.002x0.125x8.0-inch) were employed to extend the test duration. Ethylene glycol diluted with the corrosive water comprised the test solution. The temperature cycling curve, shown in the upper left of Figure 10, was repeated each 24 hours of test. The test unit was placed in a constant temperature bath and held at 77 C with constant aeration for six hours. The test unit was then removed from the
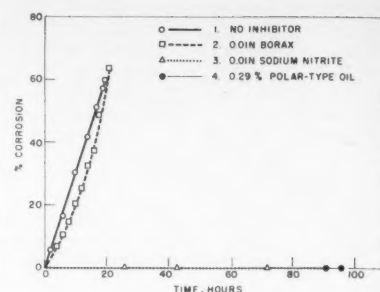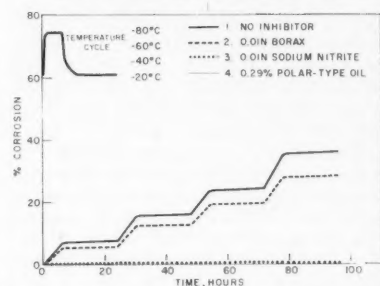
oil bath, aeration was discontinued, and the temperature gradually lowered to room temperature (24 C) under quiescent conditions.

The corrosion rate of mild steel under these cycling conditions is shown by Curve 1. The corrosion rate is expectedly higher in the hot aerated solutions than under the cooler quiescent testing conditions. Borax (0.01N) does not inhibit corrosion under these conditions (Curve 2). Sodium nitrite (0.01N) maintains adequate protection, as shown by Curve 3. The polar-type oil (.29 percent by weight), described previously, provided equally good protection (Curve 4). Temperature compensated specimens are better suited for such testing conditions. Use of mild steel probes and an improved electrical resistance corrosion measuring device under identical testing conditions produced essentially identical results.

Aluminum

Uninhibited Ethylene Glycol Solutions. The corrosion rate of aluminum in aerated 33 percent ethylene glycol-distilled water solution at 77 C is low. This

TABLE 4—Corrosion of Aluminum in 33% Ethylene Glycol Diluted With Distilled Water Containing 100 ppm Cl, SO₄, and 200 ppm HCO₃

Inhibitor	Test Duration Hours	Percent Corrosion	
		Resistance Changes	Weight Loss
No Inhibitor..	3.5	25.2	24.1
	96.0	59.1	42.6
	76.8	58.6	52.7
0.01N Borax..	100.5	27.1	24.0
0.01N Sodium Benzoate...	20.5	59.1	53.8
0.01N Sodium Nitrite.....	22.1	61.6	57.6
0.01N Sodium Silicate....	347.6	30.8	14.5
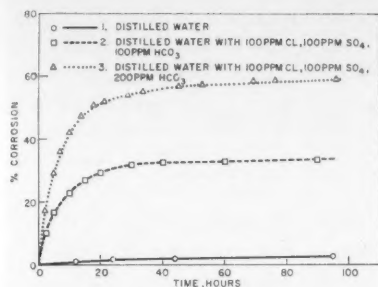
Figure 11—Corrosion of aluminum in glycol-"corrosive" water solutions.
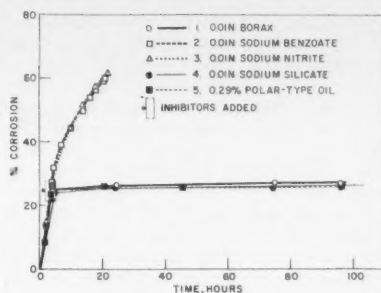
Figure 12—Corrosion of aluminum in glycol-"corrosive" water solutions with corrosion inhibitors.
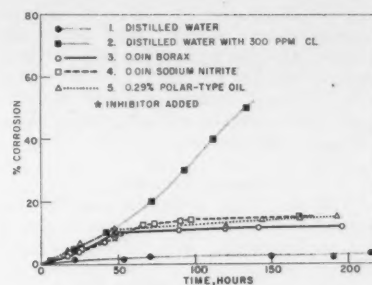
Figure 13—Corrosion of brass in glycol-"corrosive" water solutions with and without corrosion inhibitors.
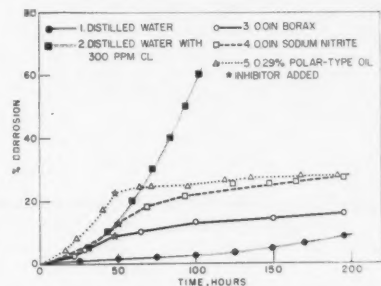
Figure 14—Corrosion of copper in glycol-"corrosive" water solutions with and without corrosion inhibitors.
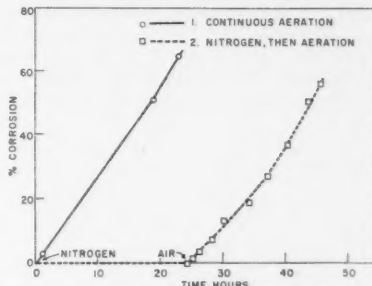
Figure 15—Corrosion of brass in glycol-water solutions with ethylene diamine.

low corrosion rate is shown by Curve 1 in Figure 11. Increasing the test duration twofold brought no increase in corrosion rate. Since additions of "inhibitors" to such a system would identify only those which accelerated corrosion, it was necessary to increase the corrosivity of the environment. Use of ethylene glycol diluted with the previously described corrosive water produced Curve 2. This corrosion rate is about 50 percent higher than that found in glycol diluted with Cleveland tap water. The aluminum corrosion rate in such a system was increased even further by an additional quantity of bicarbonate ion. The corrosion rate of aluminum in ethylene glycol (33 percent) diluted with distilled water containing 100 ppm of chloride, 100 ppm of sulfate and 200 ppm bicarbonate ions (all as the sodium salt) is shown by Curve 3. This corrosive environment was employed to examine relative corrosion inhibitor effectiveness. Pitting type of attack along with perforations occur when 0.001-inch aluminum foil corrodes under the test conditions illustrated by Curve 3. This type of attack is distributed randomly upon the specimen in such a way that there is reasonably good correlation of resistance changes and weight losses.

Inhibited Ethylene Glycol Solutions. Figure 12 illustrates the behavior of a number of corrosion inhibitors under the conditions of this test. Borax (0.01N) decreased the corrosion rate to a very low value, presumably due to its buffering capacity (Curve 1). Sodium benzoate (0.01N) and sodium nitrite (0.01N) did not stop corrosion as shown, respectively, by Curves 2 and 3. Sodium metasilicate (0.01N) provided adequate protection (Curve 4). The polar-type oil (0.29 percent by weight) provided adequate metal protection (Curve 5) without altering the pH of the system.

Some typical results regarding correlation of resistance changes and weight losses are shown in Table 4. These experiments were terminated at various times. The inhibitors were added after 25 percent ± 3 percent of the specimen had been lost due to corrosion. Incomplete removal of the adhering silicate and corrosion products is believed responsible for the low weight loss involved when sodium metasilicate was added to the corroding media.

Brass

Uninhibited Ethylene Glycol Solutions. The initial corrosion rate of brass in 33 percent ethylene glycol diluted with distilled water is relatively low, and is illustrated by Curve 1 in Figure 13. Use of glycol diluted with the corrosive water employed in the mild steel experiments (100 ppm each of chloride, sulfate, and bicarbonate ions) produced no increase in the corrosion rate. Increasing the corrosive anion contents twofold and threefold produced no increase in the rate within the time interval studied (150 hours). Brass is, however, attacked in the presence of relatively large quantities of chloride ion. The corrosion rate of brass in 33 percent glycol diluted with water which contains 300 ppm chloride ion (as the sodium salt) is illustrated by Curve 2. Subsequent experiments indicated that both the sulfate and bicarbonate ions were functioning as corrosion inhibitors for brass in the presence of the relatively corrosive chloride ion. Curve 2 represents the average values of four experiments. Due to localization of attack by the chloride ion plus incomplete removal of corrosion products, the resistance values indicated approximately 35 percent greater corrosion than shown by weight losses.

Inhibited Ethylene Glycol Solutions. The corrosion rate of brass in 33 percent ethylene glycol in distilled water which contains 300 ppm chloride ions plus added inhibitors is shown in Figure 13. Addition of sufficient borax to the corrosive solution to produce a 0.01N solution at 48 hours of test is illustrated by Curve 3. Addition of an equivalent concentration of sodium nitrite (0.01N) under identical conditions is shown by Curve 4. The polar-type oil (0.29 percent by

weight) was also effective in decreasing the corrosion rate as shown by Curve 5. Thus, all three of the corrosion inhibitors examined provided protection to brass under these testing conditions.

Copper

Uninhibited Ethylene Glycol Solutions. The corrosion rate of copper in 33 percent ethylene glycol in distilled water is relatively low. This low corrosion rate is shown by Curve 1 in Figure 14. Addition of sufficient quantities of the chloride, sulfate and bicarbonate ions to the distilled water to produce total concentrations of 300 ppm each did not produce a significant increase in the corrosion rate within the time interval of the test. Addition of the chloride ion to 300 ppm concentration produced a corrosive environment. Copper corrosion in ethylene glycol diluted to 33 percent with distilled water which contained 300 ppm chloride ion (as the sodium salt) is illustrated by Curve 2. Curve 2 represents the average of four separate experiments.

Copper corrosion under these testing conditions was found to be somewhat erratic. Reproducibility was poor due to frequent localization of attack. Correlation of resistance changes and weight losses was poor as the frequency of localized attack increased. It is felt, however, that an efficient corrosion inhibitor should either stop metal corrosion or considerably decrease the metal corrosion, whether the corrosion is general or localized.

Inhibited Ethylene Glycol Solutions. Addition of corrosion inhibitors to the corrosive environment represented by Curve 2 is shown by the subsequent curves in Figure 14. Addition of sufficient borax to produce a 0.01N solution at 48 hours of test produced a decrease in the corrosion

rate as illustrated by Curve 3. Sodium nitrite (0.01N) provided some protection (Curve 4). The polar-type oil (0.29 percent by weight) also decreased the corrosion rate as illustrated by Curve 5. Complete protection was not achieved by these corrosion inhibitors.

Special Problems

The resistance technique can be employed to advantage in investigating special problems. For example, rapid changes in the corrosivity of a given environment are easily detected by use of the resistance technique. Cuprous metals frequently have high corrosion rates in the presence of specific nitrogen-containing materials. The high corrosion rate of brass in glycol-distilled water solutions containing 0.57 percent by weight of ethylene diamine is shown by Curve 1 in

Figure 15. When nitrogen was substituted for the usual forced aeration, the very low initial corrosion rate shown by Curve 2 was observed. The usual forced aeration rate was resumed at 24 hours of test with the resulting immediate increase in corrosion rate. Weight loss measurements of the brass specimen at the end of the test used in Curve 1 showed 59 percent corrosion while resistance changes showed 65 percent corrosion. Weight loss measurements for the brass specimen illustrated by Curve 2 at the end of the test showed 56 percent corrosion by resistance changes and 55 percent corrosion by weight loss.

References

1. J. S. Dunn. *Proc. Roy. Soc.* (London), A111, 210 (1926) May.
2. N. B. Pilling and R. E. Bedworth. *J. Inst. Metals*, **29**, 529 (1923).
3. A. Dravnieks. *J. Am. Chem. Soc.*, **72**, 3761 (1950) Aug.
4. R. M. Burns and W. E. Campbell. *Trans. Am. Electrochem. Soc.*, **55**, 271 (1929) May.
5. A. Dravnieks. *Ind. Eng. Chem.*, **43**, 2897 (1951) Dec.
6. A. Dravnieks and H. A. Cataldi. *Corrosion*, **10**, No. 7, 224 (1954) July.
7. G. A. Marsh and E. Schaschl. *Oil and Gas J.*, **54**, 135 (1955) Nov.
8. W. L. Terrell and W. L. Lewis. *Corrosion*, **12**, No. 10, 491t (1956) Oct.
9. G. A. Marsh and E. Schaschl. *Corrosion*, **12**, No. 11, 534t (1956) Nov.
10. W. L. Denman. *Corrosion*, **13**, No. 1, 43 (1957) Jan.
11. E. Schaschl and G. A. Marsh. *Corrosion*, **13**, No. 4, 243t (1957) April.
12. G. A. Marsh and E. Schaschl. *Corrosion*, **14**, No. 3, 155t (1958) March.
13. A. J. Freedman, E. S. Troscinski and A. Dravnieks. *Corrosion*, **14**, No. 4, 175t (1958) April.
14. L. C. Rowe. *Corrosion*, **13**, No. 11, 750t (1957) Nov.
15. J. C. Hudson. *Proc. Phy. Soc.*, **40**, 107 (1928) Feb.
16. R. A. Powers and J. C. Cessna. Role of Polar-Type Oil Inhibitors in Promoting and Maintaining Passivity of Metal Surfaces, a paper presented at the 129th meeting of the American Chemical Society, Dallas, Texas, April, 1956.

Effect of Silicon on High Temperature Oxidation Of Stainless Steels*

By JOHN F. RADAVICH

Introduction

MANY oxidation experiments with various alloys have been carried out in order to determine the effects of alloying additions on the growth of the thin oxide film and oxide nodules.[1-7] However, very little work has been carried out on the role played by minor elements in high temperature oxidation. Work done thus far indicates that minor elements influence oxide film growth by changing the conditions of the metal-oxide interface which alters the diffusion rates of the various elements. In particular the silicon content of ferritic stainless steels seems to play an important part in adherence of oxide films and minimum pitting of alloys oxidized at high temperatures.[8]

In order to study the effects of silicon on oxidation more closely, a series of 16 Cr-10 Ni-bal Fe stainless steels with silicon contents of 0.17, 0.27, 0.42, 1.06, 1.71 and 3.55 percent were obtained.

Experimental Procedures

From the ½-inch diameter alloy bars, samples of ¼ inch thickness were cut, paper polished and electropolished in an alcohol-perchloric acid solution. Six samples were placed in a quartz crucible and the crucible was inserted in a furnace preset for 600 C. At the end of the desired oxidation interval, the samples were removed from the furnace and allowed to cool in air, examined optically, and reflection electron diffraction patterns were taken of the surface by a cold cathode electron diffraction apparatus. The same set of samples was then re-oxidized for additional periods of time and similar reflection electron diffraction examinations were carried out on the surface films.

Other sets of samples were oxidized in a similar fashion and the surfaces were examined with an electron microscope. Next, the oxide films were electrolytically stripped from the base metal. Parts of the stripped oxide film were used for electron microscopy in transmission, electron diffraction in transmission, X-ray diffraction, and X-ray fluorescent analysis studies. The descriptions and limitations of these various techniques will not be given here since they have been described elsewhere.[9]

Samples were oxidized for 5, 30 and 90 minutes at 600 C and for 5 and 30 minutes at 800 C. In addition to these temperatures, the samples were oxidized for 10 hours at 1000 C in order to correlate if possible oxide film growths and oxide scale formation at the higher temperature.

★ Submitted for publication February 2, 1959. A paper presented at the 15th Annual Conference, National Association of Corrosion Engineers, Chicago, Ill., March 16-20, 1959.

A. Discussion of Results of Film Studies at 600 and 800° C

1. Electron Microscope Study

The oxide film growth on this group of stainless steels was found to consist of a formation of a thin oxide film on top of which oxide nodules nucleate and grow. As the oxidation time increases, the oxide nodules grow in size and eventually coalesce.

Figures 1 through 9 show the oxide growth after 5, 30, and 90 minutes at 600 C on Samples 1, 4 and 6. In the initial 5-minute oxidation, a temper colored film of about 200 Å thickness is first formed. Electron microscope examination shows that there is a formation of oxide growths or nodules on the external surface. The sizes of the nodules vary from about 1/6 micron on Sample 1 to less than 1/10 micron on Sample 4 to no detectable signs of nodules on Sample 6. There are approximately 10^9 nodules/cm² on Sample 1 and 10^8 on Sample 4. As the samples are oxidized for longer periods of time, the oxide nodules grow in size and simultaneously new nodules form as shown in Figures 2, 3, 5, 6, 8 and 9. The oxide nodules eventually coalesce to form a rough oxide layer. This coalesced layer is the beginning of the usual oxide scale. As the amount of silicon increases, the number and amount of oxide nodules decreases to such an extent that the oxide scale formation is greatly retarded.

The oxide film formation at 800 C is similar to that found at 600 C except that the film formation is greatly accelerated. Figures 10 and 11 show the stripped oxide films of Samples 1 and 6 respectively after 90 minutes at 600 C while Figures 12 and 13 show the initial oxide film on Samples 1 and 6 after 5 minutes at 800 C.

Because of the greater resolution of the oxide films as replicas over plastic surface replicas, a study of the structures found in the stripped films was carried out in greater detail. It was found that the base film thickness increased by a factor of 2 or 3 from the initial to the final oxidation time while the greatest change occurred in the growth of the oxide nodules.

2. Reflection Electron Diffraction

Reflection electron diffraction (RED) studies of the oxide film formed at 600 C showed that the nodules are of the rhombohedral type, i.e. αFe_2O_3, Cr_2O_3, or a solid solution of Cr_2O_3 in αFe_2O_3 since the accuracy of this method precludes any more definite identification. The initial oxide film is oriented with the (111) planes parallel to the metal surface. As the nodules continue to grow in size, the orientation effect decreases due to the masking of the substrate film

Abstract

Growth of oxide films at 600 and 800 C on a series of 16 Cr-10 Ni-bal Fe stainless steels with silicon contents ranging from 0.17 to 3.55 percent was studied by electron microscopy, electron diffraction, X-ray diffraction and X-ray fluorescence analysis techniques. Oxide scales and sub-scales formed during oxidation at 1000 C were studied optically in cross section as well as by X-ray diffraction and fluorescence analysis.

Results show that as silicon content increases oxidation resistance increases rapidly until at the high silicon level, 3.55 percent, a very thin oxide film is formed at 600 and 800 C and very little oxide scale forms at 1000 C.

Mechanism of oxidation resistance imparted by silicon appears to be that it decreases the number of defects in the initial oxide films formed at the metal-oxide interface. With a lesser number of defects in the thin film, an enrichment of Cr at the metal-oxide interface and in the oxide films occurs and the rate of diffusion of iron outward to form the oxide scale is greatly retarded. **2.3.7**

About the Author

JOHN F. RADAVICH—Assistant professor of physics at Purdue University. He attended Missouri School of Mines and obtained a PhD from Purdue University in 1953. In 1955 he studied at the Department of Metallurgy, Cambridge University on a National Science Foundation Fellowship. His fields of interest are high temperature oxidation and structure studies using electron microscope, electron diffraction and X-ray diffraction techniques. He is a member of the ASM, AIMME, Sigma Pi Sigma, Sigma Xi, and the Electron Microscope Society of America.

by the nodular projections. Thus, the growth of the oxide nodules seems to occur in a random way. However, tilted electron diffraction studies of the thin film indicate that the orientation persists in the thin film through the 90 minutes of oxidation at 600 C.

The RED results of 5 and 30 minutes oxidation at 800 C are similar to those found at 600 C except that a weak spinel pattern is also noted after 5 minutes' oxidation on Samples 4, 5 and 6. This spinel pattern is found only on Sample 6 after 30 minutes of oxidation. This indicates that at the higher temperature the top of the thin oxide film is of spinel type material while the growing nodules are primarily of rhombohedral structure. It is probable that the spinel material is present on the surface of all samples but that the nodular projections shield the smooth surface
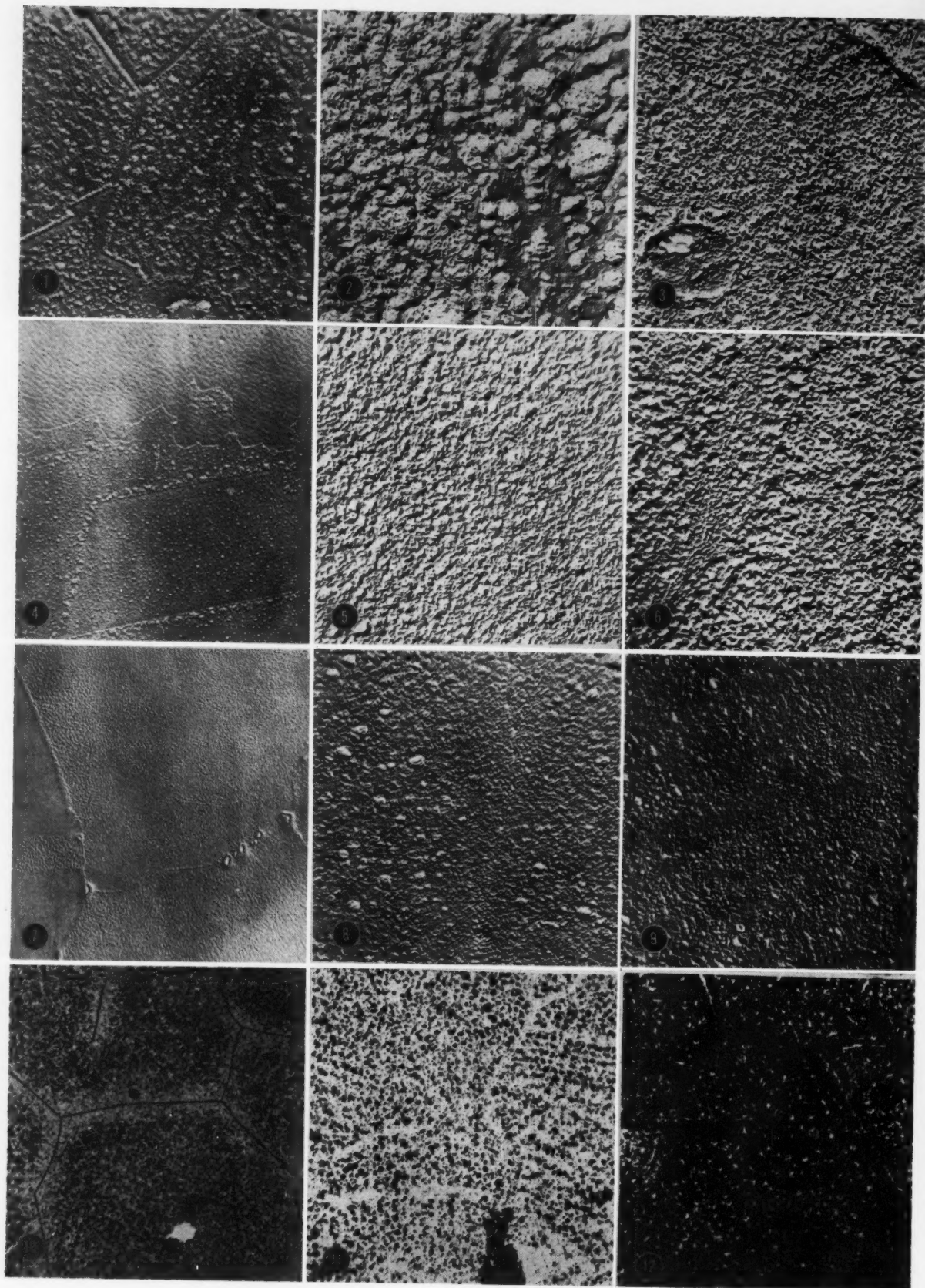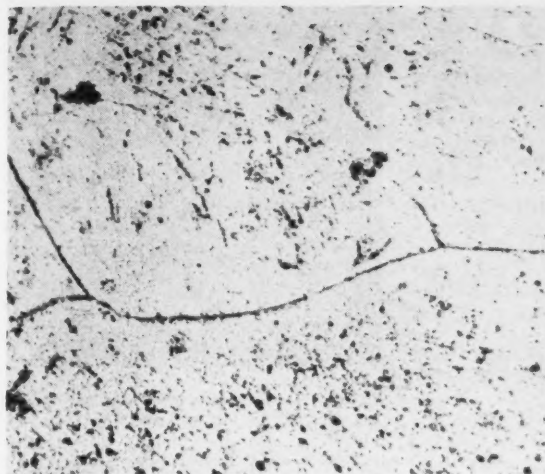
Figure 13—Stripped oxide film formed on Sample 6 after 5 min at 800 C. 3000 X
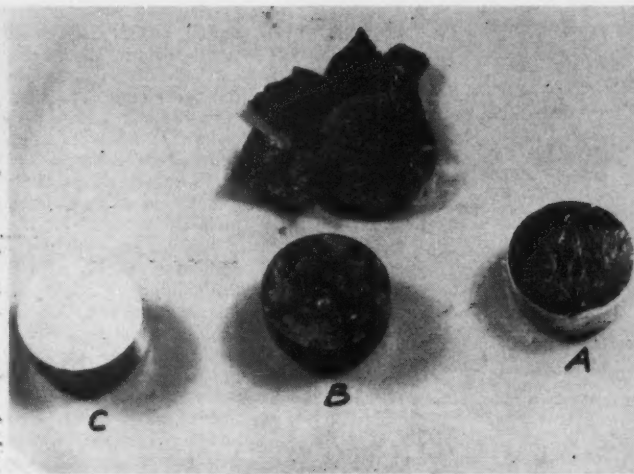
Figure 14—Effect of 10 hours oxidation at 1000 C. 2 X. (A) As electropolished (B) Sample 1 (C) Sample 6

from the electron beam. In Samples 6 appreciable amounts of substrate are still free of nodules.

3. *Transmission Electron Diffraction*

Studies of the stripped thin films by transmission electron diffraction (EDT) showed a rhombohedral structure. Measurements of the patterns gave only αFe_2O_3 but the accuracy of the measurements allows about 25 percent Cr_2O_3 to be in solid solution with αFe_2O_3 and not be detected. In most cases a weak spinel structure also was detected in both oxidation temperatures but the pattern was too faint to allow reliable lattice parameter measurements.

The appearance of a spinel phase by EDT substantiates the data obtained by RED. Since a spinel pattern was obtained by RED at the 800 C oxidation temperature and a faint spinel was obtained by EDT, it can be stated that a small amount of spinel phase is present near or on the surface of the thin films, but the majority of the thin film is of the rhombohedral type.

4. *X-ray Diffraction of Thin Films*

The results of the X-ray diffraction studies of the thin films formed at 600

and 800 C on Samples 1, 4 and 6 are given in Table 1. Alpha Fe_2O_3 was the principal phase present in the oxide films of the samples except in the case of Sample 1 in which a spinel phase was found at 600 C. The lattice parameter of this spinel phase was found to be 8.38kX units, probably Fe_3O_4.

The X-ray data are primarily of the oxide nodules because they constitute most of the volume of the oxide film. The spinel phase found by X-ray diffraction in the case of Sample 1 must be contained in the nodules and is not necessarily the same spinel as found by RED or EDT.

5. *X-ray Fluorescent Analysis*

The XFA results of the oxide films formed at 600 and 800 C are given in Table 1. These results indicate that the main portion of the films are iron with lesser amounts of Cr and some Ni. The ratios of the Fe $K\beta$/Cr $K\alpha$ indicate that the amount of Cr increased with increasing silicon content at all oxidation times but most noticeably after longer times at 600 C. The values of the Fe to Ni ratios were erratic and there appeared to be more Ni at the higher temperature.

XFA results are obtained for only Samples 5 and 6 after 30 minutes at 800 C because these samples were resistant to oxidation and therefore exhibited a characteristic film growth at this temperature.

Because XFA results are mostly of the bulk material, these data substantiate the X-ray results of strong αFe_2O_3.

B. Discussion of Results of Oxidation at 1000 C

1. *Optical Microscope*

Examination of samples oxidized for 10 hours at 1000 C showed that the lower the silicon content the greater the amount of scale which forms and then spalls from the surface upon cooling. Figure 14 shows the condition of the as-polished sample (A) with Samples 1 (B) and 6 (C) after 10 hours' oxidation at 1000 C. It is evident that the at-

tack on Sample 6 is very slight while Sample 1 not only has large amounts of oxide scale spalled from the surface but also a thick inner oxide layer still remaining on the metal. Thickness of the inner layer on the samples is dependent directly on the amount of silicon in the alloy.

In order to make comparisons of the amount of oxide still on the surface, the oxide layers were polished in cross section. Figures 15, 16, 17 and 18 show the oxide layers still on Samples 1, 2, 3 and 5. Not only does the inner layer depend on the silicon content but the amount of internal oxidation decreases as the silicon increases. No cross section micrograph was taken for Samples 4 and 6 because the amount of oxide formed on the surface (on Sample 6) was too small to retain while Sample 4 was damaged in the process of cross section mounting.

Spalled oxide scale was ground into a powder for X-ray and XFA studies. In addition, the external surface of the inner oxide remaining on the metal was scraped lightly for XFA study.

The inner oxide layer was analyzed in place by means of XFA. The oxide was then ground down on emery paper and re-examined by XFA. This method of analysis was carried out until the base metal was reached. The XFA data in the form of ratios of the Fe $K\beta$/Cr $K\alpha$ and Fe $K\beta$/Ni $K\alpha$ were calculated and are shown on the schematic diagrams.

2. *XFA of the Outer Oxide Scale*

The XFA of the ground-up scale which came off of the samples showed decreasing Fe or increasing Cr contents as the silicon content increased. The ratios of the Fe to the Cr ranged from 5.8 to .08 in Samples 1 and 6 respectively.

XFA analysis of the scraped outer surface of the inner layer showed the Cr and Ni contents to be higher than in the spalled scale. Thus the concentration of the Cr and Ni seems to be at the bottom part of the spalled layer or the outer surface of the inner layer.
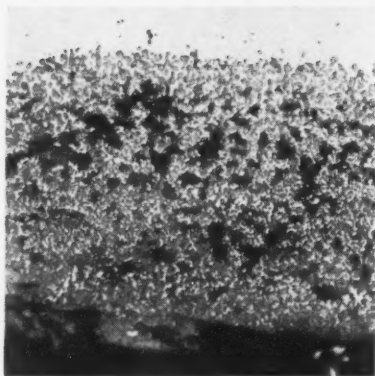
Figure 15—Cross-section of inner oxide scale formed in 10 hours at 1000 C on Sample 1. 500 X

Schematic diagrams for the six samples with XFA and X-ray results indicate clearly the changes which occur in the chemical composition of the oxide scales formed at 1000 C.

3. XFA of the Inner Oxide Scale

In order to fully understand the depletion and enrichment of elements oc-

curring because of high temperature oxidation, a detailed chemical and structural analysis should be simultaneously carried out on the various portions of the oxide scales and interfaces. This is a very difficult and time consuming procedure. However, a rough chemical analysis can be obtained by means of XFA of the same specimen before and after removal of oxide or metal layers on the metal.

The picture of the changes of the amount of Fe, Cr, and Ni at the metal-oxide interface is similar in all samples except Sample 6. As the inner layer of oxide scale is removed by grinding and the metal-oxide interface is approached, the Ni and Cr contents remain at nearly the same high values while the Fe content is much lower. Upon grinding into and through the interface, the Cr and Ni contents continue to drop to the value of the base metal while at the same time the Fe content increases. A very drastic grinding step is necessary before the base metal composition is reached in Sample 1 and 2, indicating that large amounts of depletion and diffusion are taking place in these two lower silicon samples.
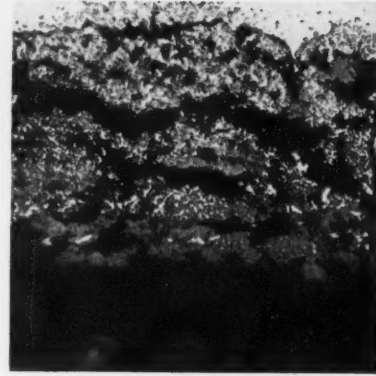
Figure 16—Cross-section of inner oxide scale formed in 10 hours at 1000 C on Sample 2. 500 X

The very high silicon content of Sample 6 prevented the formation of a volume of oxide scale sufficient for XFA and X-ray studies; however, small amounts of the surface were scraped off for XFA and X-ray samples. The results of the XFA showed a very high Cr content, nearly twice that of Fe. As the base metal was further analyzed by XFA,
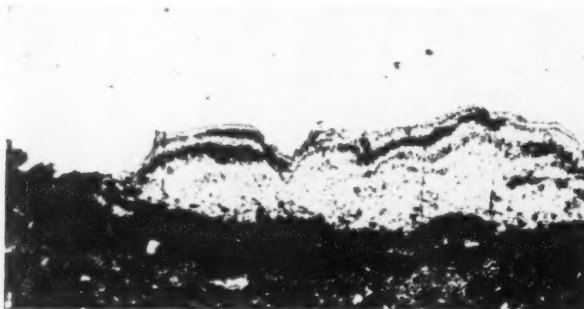
Figure 17—Cross-section of inner oxide scale formed in 10 hours at 1000 C on Sample 3. 200 X
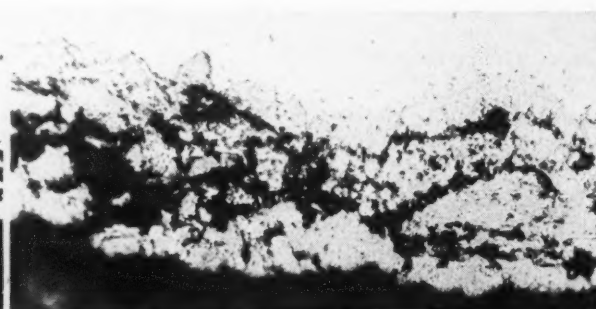
Figure 18—Cross-section of inner oxide scale formed in 10 hours at 1000 C on Sample 5. 500 X

TABLE 1—Chemical and Structural Analysis of Thin Films

Sample No.	Treatment	XFA Fe Kβ / Cr Kα	XFA Fe Kβ / Ni Kα	Elec. Dif. Trans.	X-ray Diff.
1	5 min at 600 C — air	2.1	5.1	αFe₂O₃ vs + S vvw	αFe₂O₃ s +S w
2	" " "	1.6	2.5	" " "	
3	" " "	1.8	2.3	" " "	
4	" " "	1.6	5.7	" " "	αFe₂O₃ s
5	" " "	.89	2.7	" " "	
6	" " "	.62	2.0	" " "	αFe₂O₃ vs
1	30 min at 600 C — air	3.7	3.8	αFe₂O₃ vs + S vw	αFe₂O₃ + S vw
2	" " "	3.2	3.7	" " "	
3	" " "	2.6	4.2	" " "	
4	" " "	2.3	5.3	" " "	αFe₂O₃
5	" " "	2.1	4.6	" " "	
6	" " "	1.86	5.2	" " "	αFe₂O₃
1	90 min at 600 C — air	6.32	3.8	αFe₂O₃ vs + S m	αFe₂O₃ vs + S vvw
2	" " "	4.4	4.4	" " "	
3	" " "	4.0	6.0	" " "	
4	" " "	2.4	4.8	" " "	αFe₂O₃
5	" " "	2.5	5.0	" " "	
6	" " "	.54	1.8	" " "	αFe₂O₃
1	5 min at 800 C — air	1.5	7.0	αFe₂O₃ vs + S vvw	αFe₂O₃
2	" " "	1.5	4.0	" " "	
3	" " "	1.3	5.0	" " "	
4	" " "	1.1	5.3	" " "	αFe₂O₃
5	" " "	1.1	5.5	" " "	
6	" " "	.54	1.8	" " "	αFe₂O₃
5	30 min at 800 C — air	2.0	2.0	αFe₂O₃ s + S s	αFe₂O₃ + S m + Cr₂O₃ w
6	" " "	.7	2.6	" " "	

XFA—X-ray fluorescence analysis in vacuum spectrograph; v-very, s-strong, m-medium, w-weak.
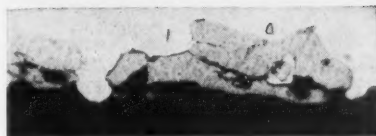
Figure 19—Cross-section of total oxide scale formed on Sample 1 after 20 hours at 700 C. Approx. 500 X

it was found that there were regions near the surface in which there was a depletion of Cr and Ni but an enrichment of Fe.

4. X-ray Diffraction Studies of the Spalled Scale

The X-ray study of the spalled scales showed large amounts of αFe_2O_3 and considerable amounts of a spinel whose lattice parameter varied from 8.38 kX (Fe_3O_4) to 8.35 kX (chromite). The outer layer of Sample 6, however, showed Cr_2O_3 with a small amount of 8.36 kX spinel. Since chromium was detected in the spalled oxide by XFA, the Cr must be in solution with the αFe_2O_3 or in the spinel or both.

C. Weight-Gain Measurements

The oxidation resistance quality of high silicon content was easily seen visually. Weight gain studies were attempted on Samples 1 and 6 after 20 hours oxidation at 700 C in order to get some quantitative values for oxidation rates. This was unsuccessful due to the spalling character of Sample 1 and the insufficient sensitivity of the apparatus to weigh the thin film which formed on Sample 6.

The nature of the oxide scale formed on Sample 1 after 20 hours at 700 C is shown in Figure 19. Although some portions of the scale had spalled from the surface, the optical micrograph shows that a thick layer is formed on this sample.

XFA studies, in the fashion described above for the 1000 C oxidation work, were carried out on Sample 1 which was oxidized 20 hours at 700 C. This work showed that the oxide layer formed at this temperature was richer in Cr and Ni than the oxide layers which spalled in the 1000 C oxidation. It was necessary to grind five times before the base metal composition was obtained. In contrast to the thick oxide scale which formed on Sample 1 at this temperature, a thin oxide film (of the order of 1000 Å) formed on Sample 6.

Conclusions

It has been found that in the initial oxidation a temper colored film of about 200 Å thickness is formed first. Surface examination by electron microscopy shows that a formation of oxide nodules or surface growths has occurred at random positions. With increasing oxidation time, the oxide nodules grow in size while new nodules form. The oxide nodules coalesce to form a rough oxide scale. While the nodules grow by a factor of at least 10, the thin oxide substrate grows by only a factor of 2 or 3.

The thin oxide film which initially
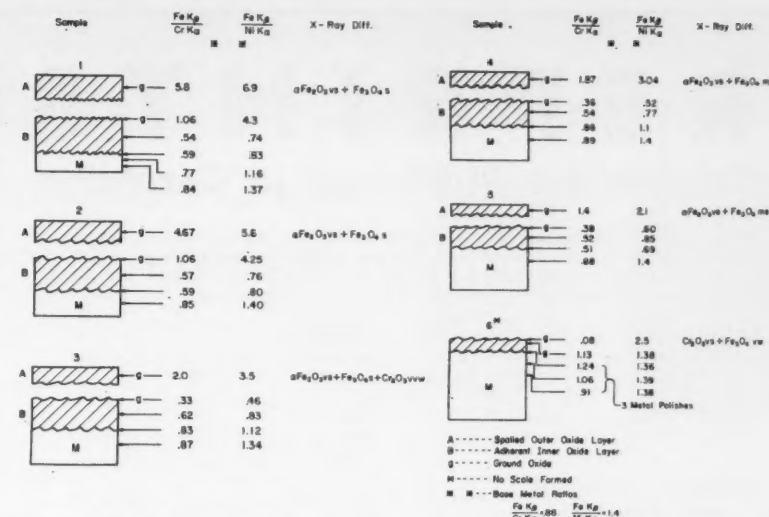
Figure 20—Schematic diagrams of inner oxide scales on Samples 1-6 with chemical and structural analysis of various layers.

forms grows in an oriented way such that the (111) planes of the rhombohedral phase are parallel to the surface of the metal. It is likely that this preferred crystal growth would introduce imperfections in the thin oxide film which would allow the iron to diffuse outward to form the oxide nodules.

An increased amount of silicon in the sample enhances oxidation resistance. As the silicon content is increased, the number of oxide nodules which form is decreased so that the uniformly thin oxide film formed first is stable for a longer period before being covered over by oxide nodules. In addition the chromium concentrates at the metal-oxide interface and retards the diffusion of iron outward. This retardation of oxide nodule formation and chromium concentration results in a low oxidation rate for the alloy.

The number of oxide nodules or imperfections decreases from a value of 10^9 per cm² for Sample 1 to 10^8 for Sample 4 to a value too low to be recorded for Sample 6 after 5 minutes' oxidation at 600 C. At higher temperatures the number of nodules seems to be the same except that growth and coalescence are greatly accelerated.

In order to impart oxidation resistance the silicon either must be in the oxide films which form or concentrated in a separate silica-rich layer at the metal-oxide interface. If the silicon is in the thin oxide film as a silica phase, it should be detected by electron diffraction or X-ray diffraction techniques used in this study. No different or unusual phases were found. If on the other hand, the silica was concentrated at the metal-oxide interface, it should be detected in cross section micrographs. No such layer was found.

The absence of a silica layer might be explained on the basis that the layer which forms at the interface is thin and amorphous. Structural techniques used in this investigation would not detect such an amorphous material. Past work

on oxidation studies of ferritic stainless steels has shown that a continuous amorphous layer high in silicon is present at the interface after 20 hours at 1000 C.[8] Other investigators have found alpha cristobalite on Type 446 stainless steels after several hundred hours at high temperatures.[10] It is possible that the short times of oxidation of this study does not allow the formation of crystalline material.

References

1. J. F. Radavich. High Temperature Oxidation of Gas Turbine Alloys, to be published.
2. J. F. Radavich. Am. Soc. Testing Materials, Special Technical Publication No. 171, p. 14 (1955).
3. R. T. Phelps, E. A. Gulbransen and J. W. Hickman. *Ind. Eng. Chem.*, Anal. Ed., 18, 391 (1946).
4. E. A. Gulbransen, R. T. Phelps and J. W. Hickman. *Ind. Eng. Chem.*, Anal. Ed., 18, 640 (1946).
5. H. J. Yearian. *Phys. Rev.*, 82, 341 (1951).
6. H. J. Yearian, W. D. Derbyshire and J. F. Radavich. *Corrosion*, 13, No. 9, 597t-607t (1957).
7. L. Horvath and J. F. Radavich. The Effects of Minor Constituents on the Oxidation of Type 446 Stainless Steel, unpublished report.
8. H. J. Yearian. Summary Technical Report, Purdue Research Foundation, Purdue University, June 1954.
9. J. F. Radavich. Am. Soc. Testing Materials, Special Technical Publication No. 171, p. 89 (1955).
10. M. Cohen and D. Caplan. *Jour. of Metals*, 4, 1057 (1952).

Summary of Information Given On Microbiological Corrosion

A summary of some of the information available on microbiological corrosion of metals was made in a report submitted by Project Group T-4B-1D on Corrosion by Microbiological Action. Most investigations have been concerned with iron and steel, but bacteria can cause corrosion of zinc, aluminum, lead, tin and other metals under anaerobic conditions.

In a review of the literature on microbiological factors involved in the corrosion of iron and steel (see *Corrosion*, 11, 442t, 1955, October) seven types of bacteria were given as influencing the corrosion process: sulfate reducing methane producing, iron bacteria, hydrogen oxidizing, sulfur oxidizing, nitrosifying bacteria. The first two are anaerobic; the others are aerobic.

Six mechanisms were listed in the article by which organisms affect corrosion:

1. Through mechanical activities such as chewing, scraping, abrading or coating metal surfaces.
2. By affecting electrochemical conditions (for example, galvanic cell action and surface changes).
3. By affecting pH or acidity.
4. By affecting redox potentials.
5. By changing the chemical composition of the environment by catalyzing the reactions involving ammonia, nitrate, nitrite, organic matter, sulfate, sulfide, carbonate, iron, manganese and other ions.
6. By affecting oxygen tension through the production or consumption of oxygen.

Seven ways bacteria affect corrosion were given Roger D. Reid's article "Microbes With an Appetite for Iron" published in the May, 1955, issue of the Navy Department Research Reviews:

1. May oxidize iron, manganese, sulfur or hydrogen sulfide.
2. Change the pH (hydrogen ion concentration) of the surface to produce acidic microspheres.
3. Cause a change in Eh or electrode potentials.
4. Create micro-galvanic cells.
5. Depolarize surfaces by oxidizing hydrogen.
6. Form films that retard diffusion of corrosive acids.
7. Induce attachment of sedentary plants and animals on solid surfaces, and these in turn permit accumulation of bacteria or other corrosive by-products.

On lead cable sheaths, anaerobic corrosion is caused by specific types of bacteria which are active in environments free of oxygen (see *Corrosion*, 9, 425, 1953, November). Other factors are moisture content, alkalinity and pH.

Corrosion of iron pipes in soil is a cyclic process in which microbiological reduction of sulfate to sulfide takes place during anaerobic conditions and oxidation of the sulfide and sulfur to sulfuric acid takes place under aerobic conditions,

according to a paper entitled "Unity of the Anaerobic Iron Corrosion Process in Soil" by C. H. A. Von Wolzogen Kuhr, presented at the 1937 Bureau of Standards International Corrosion Conference held in Washington, D.C.

Oxidizing or reducing intensities of soils, computed from electric potential difference between a platinum electrode and a calomel reference electrode, were correlated with the corrosiveness of the soil in field tests given in an article by F. E. Costanzo and R. E. McVey (*Corrosion*, 14, 268t, 1958, June).

Utility Industry Corrosion Discussed At T-4F Meeting

Corrosion problems of utility industry other than with water were discussed by Technical Committee T-4F (Materials Selection for Corrosion Mitigation in the Utility Industry) at its Chicago meeting.

The use of epoxies with a fine sand for an abrasive and use of uncoated ductile iron were suggested to solve corrosion problems where coal tar materials had not been satisfactory on metal in steam manholes.

Protection of traveling screens at power plant intakes also was discussed. One committee member credited impressed current cathodic protection for preventing corrosion. Calcarious deposit formation was cut by control of the current input. Mild steel and graphite anodes were used. Vinyl coatings were used on some screens to decrease the current requirements. Some graphitization occurred on cast iron sprockets. The system required complete isolation of all metal.

Compton   Rowe

NEW OFFICERS recently elected for Technical Group Committee T-4D on Corrosion by Deicing Salts are Chairman K. G. Compton, Bell Telephone Laboratories, Murray Hill, N.J., and Vice Chairman L. C. Rowe, General Motors Corp., Detroit, Mich. Mr. Rowe also has been elected vice chairman of Group Committee T-3 on General Corrosion.

The committee also discussed protection of cast iron condenser water boxes. Impressed currents and sacrificial zinc anodes have been used to provide cathodic protection. Current requirements have been high and in some cases resulted in graphitization of the cast iron. Bronze has been used instead of cast in a few cases.

A report from Task Group T-4F-1 (Materials Selection in the Water Industry) was given on the groups current work on problems associated with water valve corrosion.

Valve manufacturers complained that they have difficulty in obtaining information on results of special valves placed in service. Users seldom report when the valve application was successful rather than a failure. Valve companies stated this was regretable because the manufacturer may have developed a special product and could expand its application if they know when applications were successful.

•

8529 copies of NACE Technical Committee Reports published in CORROSION were sold in 1957.

Membership in NACE Technical Unit Committees

A question frequently asked by guests attending meetings of Technical Unit Committees is "How may I become a member of this committee?" This question is answered in the following procedure quoted from the Technical Committee Operation Manual:

1. Any member of NACE (irrespective of place or country of residence) may become a member of a Technical Unit Committee upon fulfillment of the following requirements.

2. He should apply in writing to the Chairman of the Unit in which he desires membership, stating his interest and willingness to participate in the activities of the

Unit and giving his experience in the subject.

3. Approval by the Chairman of the Unit Committee of the application or by majority vote of committee members by letter ballot is necessary for appointment of an applicant to membership in a Unit Committee.

4. The Chairman of the Unit Committee will notify each applicant of his acceptance or rejection.

A directory of NACE Technical Unit Committees and Officers is published in the January, April, July and October issue of CORROSION.

77% of T-8 Membership Attends Chicago Meeting

Seventy-Seven percent of the membership was present at the Chicago meeting of Technical Committee T-8 (Refining Industry Corrosion) held during the annual conference. A total of 121 persons attended the all-day meeting.

Six new members were listed since the October, 1958, meeting in New Orleans.

Reports from Task Group T-8A and T-8B were given during the meeting. Other topics discussed included the papers presented at the Refining Industry Symposium at the Annual Conference, corrosion in reforming and desulfurization units, naphthenic acid corrosion, corrosion of exchangers and condensers, corrosion during down-time, metallurgy phenomenon of interest, corrosometer applications and waterside corrosion problems.

New topics discussed and to be continued at the next meeting during the South Central Region Conference (Denver, Oct. 12-15) were corrosion of welds on Type 347 stainless steel, hydrogen attack on iron and corrosion problems resulting from use of oxygen addition in a catalytic cracking regenerator.

Task Group T-1H-4 Meets

Task Group T-1H-4 (Oil String Casing Corrosion, West Coast Area) met May 25-27 to conduct tests to find a valid method of testing for cathodic protection interference on oil well casing that would not interfere with production of the well.

A pipe line was selected to represent the well casing. Simultaneous measurements were made along the pipe to determine whether there is any correlation between two measurements for finding interference and determining when it is eliminated.

Nine companies participated in the tests made in the Rio Bravo Oil Field, Kern County, Cal.

T-6D Hears Group Report

Technical Committee T-6B (Protective Coatings for Resistance to Atmospheric Corrosion) heard a preliminary report from its Task Group T-6B-11 on Metallic Silicates at the meeting held during the Annual Conference in Chicago.

Copies of the report were given to committee members for comments and criticisms.

A new Task Group T-6B-17 on Chemical Cured Coal Tar Coatings was established by committee vote. W. E. Kemp was appointed chairman of the new group.

Approval was also given to a format outline for task group reports.

T-3F Discusses Projects

Research projects which NACE might sponsor were discussed at the Chicago meeting of Technical Unit Committee T-3F on Corrosion by High Purity Water. One such project was the need for knowledge of pH and dissociation phenomena in aqueous media at high temperature and pressure.

The committee decided that papers should be solicited for future symposia on high purity water corrosion so that a broader audience could be attached to the symposium meetings.

2 Task Group Reports Are Given at T-1K Meeting

Two task group reports were given at the Chicago meeting of Technical Unit Committee T-1K on Inhibitors for Oil and Gas Wells. Task Group T-21K-1 on Sour Crude Inhibitor Evaluation reported that work has been completed on a revised static corrosion test procedure and has been submitted to the Technical Practices Committee. A proposed dynamic test also has been prepared by T-1K-1. Its test procedure is broad and covers all tests now used by various laboratories engaged in inhibitor work. In general, this test is more severe than the standard static test and probably will screen out inhibitors passed by the static test.

Task Group T-1K-3 on High Temperature Corrosion Inhibitors will consider problems related to high temperature hydrochloric acid corrosion. in producing wells. Only 9 companies out of 30 contacted have indicated interest in such a project.

The scope of Task Group T-1K-2 on Sweet Corrosion Inhibitors have changed to include work on film persistency, rock adsorption and retention and tests at high concentrations.

New Task Group Appointed On Interference Problems

Technical Unit Committee T-1H at its last two meetings in New Orleans and Chicago, on Oil String Casing Corrosion, discussed interference problems on wells with cathodic protection and appointed Jack Battle, Humble Oil and Refining Co., Houston, as chairman of a new task group to study this problem.

A test was discussed in which existing pipelines are used to stimulate a casing interference problem. Results may be completed for a later report. One committee member suggested that a definite negative shift in potential will exist if there is interference and that anode location is critical in minimizing interference effects.

Also discussed by the committee were possible means of determining the amount of external corrosion of well casing. Members reported that several companies are working on such a tool which should be available in about a year. One company was reported working on a magnetic flux density tool for measuring casing damage.

T-1B Meeting in Chicago

Work done by companies in studying plastic coated tubing was discussed by Technical Unit Committee T-1B (Condensate Well Corrosion) at its Chicago meeting. In these studies, coatings were exposed to environments of H_2S gas, caustic mud, distilled water and mud acids at temperatures to 350 F and 10,000 psi. Some companies indicated a correlation between poor coating application and holidays in the coatings.

Ab
Pe

Abo
8th B
by the
tember
were
dustry
organi

Ove
in 60
in th
busses
miles.

A r
sent t

The
tendan
Permi
tours
oil in
about
Permi

Illi
So

The
Corro
Unive
Elect
Meta
tion w
7-11
pus a

Sev
ing s

All
Illini
neeri
neeri

Wa
of U
engin
eral
men
ger,
facul

Re
inclu
cours
eons
meal

Ac
shou
neeri
725

A
give

NACE NEWS

About 200 Engineers Attend Permian Basin Corrosion Tour

About 200 persons registered for the 8th Biennial Corrosion Tour sponsored by the Permian Basin Section held September 23-25. Most of the registrants were engineers from the petroleum industry and related service and supply organizations.

Over 300 pieces of oil field equipment in 60 different exhibits were included in the tour made by air conditioned busses over approximately 3000 square miles.

A report of the corrosion tour, to be sent to all registrants, is being prepared.

The first tour was in 1947 with attendance limited to members of the Permian Basin Section. In 1949 the tours were opened to any person in the oil industry. In this year's registration, about 40 percent was from outside the Permian Basin area, according to Jack Ward, Plastic Applicators, Inc., Midland, who was chairman of the tour.

Other persons helping in the tour were Bob Weeter, Magnolia Petroleum Company, Midland, in charge of exhibits; Roscoe Jarmon, Permian Enterprises, Midland, in charge of indoor displays; Clovis F. Kendrick, Tex-Tube Inc., Midland, in charge of publicity; Bill Bayless, Sivalls Tanks, Inc., Odessa, in charge of tour guides; and Ed Moses, Plastic Applicators, Inc., Midland, in charge of arrangements.

Permian Basin Section officers also helped in conducting the tours. They are Chairman Roscoe Jarmon, First Vice Chairman, Kirk A. Harding, Gulf Oil Corp., Goldsmith, Second Vice Chairman R. C. Booth, Plastic Applicators, Inc., Odessa, Secretary-Treasurer R. F. Weeter, and Trustee John Gannon, Texaco Inc., Midland.

Illinois Corrosion Short Course Scheduled for December 7-11

The 4th Biennial Short Course on Corrosion Control conducted by the University of Illinois Department of Electrical Engineering and Mining and Metallurgical Engineering in cooperation with NACE will be held December 7-11 on the University of Illinois campus at Urbana.

Several NACE members will be visiting speakers during the short course.

All sessions will be conducted in the Illini Union Building, Electrical Engineering Building and Electrical Engineering Research Laboratories.

Walter H. Bruckner, NACE member of University of Illinois metallurgical engineering research professor, is general chairman of the course. Co-chairmen are H. N. Hayward and M. Metzger, both of the University of Illinois faculty.

Registration is $55 per person which includes text materials, copy of the short course proceedings, five scheduled luncheons and a banquet. Lodging and other meals are not included.

Advance registration is requested and should be sent to Supervisor of Engineering Extension, 116-D Illini Hall, 725 South Wright St., Champaign, Ill.

A schedule of the short course is given below:

Monday, December 7

Registration (8-9:30 am)
Welcoming Address: R. J. Martin, University of Illinois.
Mathematics of Finance, by L. B. Archer, University of Illinois.
Basic Corrosion Theory, by M. Metzger and B. C. Rickets, University of Illinois.
Elements of Circuit Theory, by H. N. Hayward and J. O. Kopplin, University of Illinois.
Smoker Session: discussion and display of different pipe specimens exposed to different water conditions in the United States and Canada, by T. E. Larson, State Water Survey.

Tuesday, December 8

Corrosion Inspection Methods in Practice, by H. C. Van Nouhuys, consulting engineer, Marietta, Ga., and L. P. Sudrabin, Electro Rust-Proofing Corp., Belleville, N. J.
Economics of Corrosion Control, by L. P. Sudrabin.
Corrosion Control, by W. H. Bruckner and M. Metzger.
Principles of Cathodic and Anodic Protection, by W. H. Bruckner.
Guided Tours to laboratories for cathodic protection, bio-physics, gaseous electronics, metallurgy and microwave research.

Wednesday, December 9

Electrical Measurements in Corrosion Control, by H. N. Hayward, University of Illinois, and Roy O. Dean, Pacific Gas and Electric Co., San Francisco, Cal.
Use of Electrical Instruments for Corrosion Control, by H. N. Hayward, Roy O. Dean and J. O. Kopplin.
Cathodic Protection Round Table Topics: pipelines and storage tanks, power and communication cables (lead sheath problems), pressure vessels and marine applications, interference from and to foreign structures.
Cathodic Protection Practices, by Marshall E. Parker, consulting engineer, Houston, Texas.
Motion Pictures: corrosion control topics.

Thursday, December 10

Plastic Coatings for Corrosion Control, by Mel Hendrickson, Minnesota Mining and Manufacturing Co., St. Paul, Minn.
Tar Coatings for Corrosion Control, by W. F. Fair, Jr., Koppers Company, Verona, Pa.
When, Where and How for Sacrificial Anodes and Rectifiers, by Marshall E. Parker.
Round Table Discussion of Coatings and Cathodic Protection Practices.
Banquet Address: F. L. LaQue, International Nickel Co., Inc., and ASTM President.

Friday, December 11

Management Objectives, by P. M. Dauten, Jr., University of Illinois.
Operation Objectives and Relationship to Management, by L. W. Ewing, Jr.
General Round Table Discussion.

•

Certificates for past chairmen of regions and sections, measuring 9 x 12 inches, are available from the Central Office at $7.50 each.

PERMIAN BASIN 8th Biennial Corrosion Tour held September 23-25 featured on-location displays and exhibits of methods used to control corrosion in the oil industry. Shown above are some of the 200 registrants who participated in the tours of oil field equipment.

Canadian Region News

Edmonton Section heard W. H. Seager of International Pipeline Company speak on the effect of temperature on current requirements for cathodic protection at the September 24 supper meeting.

The section will hold its regular meeting on November 26 at the Corona Hotel.

•

Montreal Section has planned to hear a speaker on new plastics at the November 10 meeting.

Other meetings have been planned for 1960: February 9 on cement corrosion and March 8 on inhibitors.

•

News intended for publication in CORROSION should be in Houston not later than the 10th of the month preceding month of publication.

•

NACE's 18th Annual Conference and 1962 Corrosion Show will be held March 18-22, 1962, at the Municipal Auditorium in Kansas City, Mo.

South Central Region News

New Method of Controlling Hot Acid Corrosion Given at Denver Conference

A method of controlling corrosion by hot oxidizing acids has been developed by researchers at Continental Oil Company's Laboratories at Ponca City, Oklahoma. This method involved application of an electrical current to the anode. The research has shown that the electrical current produces an oxygen film on the surface which in some cases almost completely prevents corrosion.

The method has been tested at the Baltimore plant of Continental Oil Company over a period of a year. The engineers believe that this method will have wide application in all chemical processes involving acidizing environments handled in mild and stainless steel.

Details of this method, its application and a potential controller which allows metal oxidation to become of immediate practical importance were presented in three technical papers at the South Central Region Conference held in Denver, Oct. 12-15. A more extensive description of the method is being prepared for publication in the December issue of CORROSION as a part of a report on the Denver Conference.

The three papers presented at Denver which gave information on this new method were as follows: "Anodic Passivation Studies," by J. D. Sudbury, O. L. Riggs and D. A. Schock; "Anodic Control of Corrosion in a Sulfonation Plant," by O. L. Riggs, M. Hutchinson and N. L. Conger; and "Application of Anodic Corrosion Control in the Chemical Industry," by D. A. Schock, O. L. Riggs and J. D. Sudbury.

The South Central Region's 13th Annual Conference at Denver attracted more than 600 persons from widely separated parts of the United States. The program proceeded smoothly throughout the four days of the meeting.

Attendance at technical committee meetings was good, and in some cases standing room only was observed. Attendance at symposia was very good.

The conference committee, in addition to providing an interesting technical program, also was congratulated on the numerous sightseeing and industrial tours made available and on the well organized entertainment program.

NACE Vice President George E. Best, Solvay Process Division of Allied Chemical Corporation, Syracuse, N. Y., was a guest at the annual business luncheon

attended by more than 500 and received a 10-gallon hat as a token of esteem from the South Central Region.

Resolutions were adopted in recognition of the contributions to NACE of the late J. C. Spalding, Jr., director for the South Central Region on NACE's board of directors.

Houston Section to Hold Two-Day Corrosion Course

The Houston Section will sponsor a two-day course in practical corrosion control systems to be held January 28-29 at Houston's Rice Hotel.

One day of the course will be devoted to fundamentals of corrosion and corrosion control. The second day will include individual full-day sessions on corrosion control systems for five industries: pipelines, utilities, commercial and residential construction, industrial and chemical plants and oil and gas production.

The course is designed for operating field men, supervisory personnel, engineers and technicians associated with corrosion problems, architects and engineers concerned with industrial and residential design and construction and for salesmen serving in the corrosion control field.

Additional information can be obtained from M. A. Riordan, P. O. Box 6035, Houston 6, Texas.

●

Panhandle Section will hold its regular meeting on November 24. The next meeting will be December 29.

New section officers recently installed are Chairman L. A. Thompson, Celanese Corporation of America, Pampa, Vice Chairman L. J. Roberts, Western Gas Service Co., Borger, Secretary-Treasurer J. F. Headrick, Phillips Petroleum Co., Phillips, and Trustee V. R. Ogilvie, Plastex Co., Borger.

●

North Texas Section has scheduled its next meeting for December 7, when new section officers will be elected.

At the September 14 meeting, C. C. Cox of Chance Vought Aircraft Corporation was the guest speaker.

●

Sabine-Neches Section will hold no meetings during November and December. The next section meeting will be January 28.

At the September 24 meeting, H. M. Wilten of Texaco's Port Arthur Refinery spoke on factors to be considered in selecting steel for high temperature applications in refineries.

Greater Baton Rouge Area Section heard Pat O'Brien of Socony Paint Company speak on practical paint problems at the September 12 meeting.

A nominating committee to select candidates for 1960 section offices was appointed: John Bankston, Solvay Division, Ed Doescher, Levingston Supply, and Douglas Speed, Esso.

March '59 Issues Of Corrosion Needed

Copies of the March, 1959, issue of CORROSION are needed to complete Volume 15 for library subscribers. Any CORROSION reader who no longer needs the March issue for reference is asked to send it to Central Office, NACE, 1061 M & M Bldg., Houston 2, Texas, attention N. E. Hamner. The issues received will be sent to library subscribers.

DEATHS

J. C. Spalding, Jr., general conference chairman for the NACE 16th Annual Conference, died in a Dallas hospital September 29 after a brief illness.

In his ten years of active participation in NACE, Mr. Spalding held many offices. He was on the Board of Directors as representative of the South Central Region at the time of his death. Other offices held during his membership included chairman of the North Texas Section and secretary-treasurer, vice chairman and chairman of the South Central Region.

In addition to holding NACE offices, he was active in the Association's technical committee work. He was chairman of Technical Committee T-1K on Inhibitors for Use in Oil and Gas Wells. He also was general chairman of the 1954 South Central Region Conference held in Dallas and had written several articles on inhibitors and corrosion control in production operations.

Spalding

Affiliated with the Sun Oil Company, Dallas, he was section supervisor of the mechanical, chemical and material and equipment engineering section. He joined the company in 1947 as field engineer working on drilling fluids and related oil production problems. He began his corrosion work in this same year and was made decision materials and equipment engineer.

Mr. Spalding also was active in the field of education. He served on the staff of the Chemistry Department at Southern Methodist University. He received a BS in chemical engineering from Georgia School of Technology and a BS in basic engineering from the same school. He also attended Texas A & M College. During World War II he served with the United States Marine Corps.

Mr. Spalding also was a member of API, AIME, ACS and AIChE.

2 NACE Members Elected New Officers of ASTM

Two NACE members have been elected officers for the American Society for Testing Materials at the society's recent meeting in Atlantic City, N. J.

Frank L. LaQue, former NACE president who is vice president of International Nickel Company's development and research division, was elected ASTM president for a one-year term.

H. D. Wilde, research coordinator for Humble Oil & Refining Co., Houston, Texas, was elected for a three-year term as one of the ASTM directors.

•

The University of Illinois Corrosion Control Short Course will be held on the Urbana Campus December 7-11.

•

News intended for publication in CORROSION should be in Houston not later than the 10th of the month preceding month of publication.

Transite Pipe is strong, lightweight, easily handled . . . only larger diameters need handling equipment.

The Ring-Tite Coupling speeds and simplifies installation . . . assures lasting protection against leakage.

Northeast Region News

Greater Boston Section has scheduled T. P. May of International Nickel Co., Inc., as guest speaker for the November 12 meeting. His topic will be relative corrosion of metals.

The section is considering sponsorship of a corrosion control short course and has mailed questionnaires in an effort to determine the amount of interest for such a short course in the Boston area and what subjects would be desirable. The section is now affiliated with the Engineering Society of New England.

Kanawha Valley Section had a two-part program on materials of construction for cooling waters at its September 24 meeting. A. S. Krisher of Monsanto Chemical Company discussed corrosion in cooling water, and John Burke of National Aluminate Corporation discussed water chemistry and treatment.

Schenectady-Albany-Troy Section has tentatively been given authority to proceed with plans for the 1962 annual meeting of Northeast Region at a place to be determined, probably Albany. The region has scheduled meetings for 1960 at Huntington, West Virginia, and at New York for 1961.

Baltimore-Washington Section will hear T. J. Maitland talk on "Problems, Testing and Mitigation Methods Peculiar to Corrosion Control of Lead Sheath Cables in Underground Ducts" at the November 16 meeting. Program chairman will be H. L. Baer.

Austin K. Long of the Glidden Company spoke on protective coatings at the section's September 22 meeting.

Pittsburgh Section held a coating roundtable discussion for its November 5 dinner meeting. Kenneth Tator was moderator; roundtable members were J. H. Cogshall, W. F. Fair, Jr., J. D. Keane and G. W. Seagren.

News Deadline for CORROSION is the 10th of each month.

North Central Region News

Chicago Section Nominates Slate of 1960 Officers

A committee was named by Ivan J. Acosta, Crane Co., Chicago Section chairman, to select a slate of officers to be voted on for the new fiscal year adopted by the section at its September 15 dinner meeting.

Named on this committee were Harold C. Boone, Peoples Gas, Light and Coke Co., Wendell A. Watkins, Duriron Co., Robert H. Weisert, Sales Engineering Inc., and Clifford N. Crowe, Standard Oil Company of Indiana. The new section year will coincide with the calendar year.

The meeting, held at the Chicago Engineers' annual ladies' night and featured a program on fire prevention by Miss Amelia Miller, Underwriters' Laboratories, Chicago. About 40 persons were present.

N. T. Shiedeler of Pittsburgh Coke & Chemical was the guest speaker at the October 20 meeting. His subject was "Coal Tar-Epoxy Resin Coatings in Industry."

Kansas City Section heard Theodore C. Hoppe speak on "Control of Corrosion at a Utility Station" for the October 12 dinner meeting.

W. W. Wright of Phillips Petroleum Company spoke on "Inspection for Corrosion Using the Audio Gauge" at the September 14 meeting.

Cleveland Section officers recently elected for 1959-60 are Chairman John Scott, Truscon Laboratories, Mentor, Ohio; Vice Chairman Peter P. Skule, East Ohio Gas Co., Cleveland; and Secretary-Treasurer W. H. Hooker, Harco, Corp., Cleveland.

Southwestern Ohio Section had Brig. General William E. Creer of the Air Force discuss SAC operation corrosion problems at the dinner held September 29. Speaker on the technical program was Fred Fink of Battelle Memorial Institute. His subject was corrosion test methods.

Detroit Section Plans Programs Through May

Announcements for the Deroit Section's meeting were typed on gum labels so that members could tear off each meeting announcement and paste it on desk calendars for reminders.

The labels contained complete information about the meetings scheduled through May, 1960, as follows: (all meetings at Engineering Society of Detroit Building).

November 19: Uses of Polyester-Fiberglass in Chemical Industry, by W. A. Symanski, Hooker Chemical Corp., Niagara Falls, N. Y.

January 21: Tank Lining—Sheet, Spray and Plated, by L. Woerner, Automotive Rubber Co., L. J. Barker, Union Carbide, and W. J. Crehan.

February 18: Joint meeting with Electrochemical Society. H. T. Francis of Armour Research Foundation will speak on "Electrochemical Mapping of Plated Surfaces."

March 24: Annual Paint Meeting. R. Gackenbach of American Cyanamil Co., New York, N. Y., will be guest speaker.

April 26: Dinner meeting concurrent with ASTM. Frank LaQue of International Nickel Co., Inc., will be guest speaker.

May 19: Dinner meeting. Forum discussion and exhibit on non-destructive testing for corrosion control.

8529 copies of NACE Technical Committee Reports published in CORROSION were sold in 1957.

Northeast Region Board
Nominates '60 Officers

J. Dwight Bird, Dampney Co., Boston, Mass., has been nominated as a candidate for the office of director representing the Northeast Region.

A nominating committee reporting to the region's board of trustees during the October 5-8 Baltimore conference also listed the following nominees:

A. F. Minor, American Telephone and Telegraph, New York, N. Y., for regional chairman. J. H. Cogshall, Pennsalt Chemical Co., Philadelphia, Pa., for vice chairman. H. H. Bennett, Socony Mobil Oil Co., Paulsboro, N. J., and J. M. Bialosky, Koppers Co., Verona, Pa., for secretaries.

A report of the committee is being mailed to members in the region.

NORTHEAST REGION's guests at its annual banquet October 6 during the 11th Annual Conference at the Lord Baltimore Hotel, Baltimore, Md., heard R. Carson Dalzell, Assistant Director, Atomic Energy Commission Washington, D. C., speak on corrosion problems in atomic energy plants.

Corrosion in Atomic Plants
Discussed at Baltimore Meeting

The vital necessity to control corrosion in atomic energy plants was explained by R. Carlson Dalzell, Assistant Director, Atomic Energy Commission, Washington, D.C., at the annual banquet of Northeast Region Tuesday, October 6, at the Lord Baltimore Hotel, Baltimore, Md. Dr. Dalzell was principal speaker at the banquet. Theodore R. McKeldin, former governor of Maryland was toastmaster.

Dr. Dalzell described some of the problems faced by scientists and engineers in the design and operation of atomic piles and other installations in which even a pinhole of corrosion could result in destruction of the pile at a cost of many millions of dollars. Aluminum casing for fuel slugs in the pile sometimes develop pinhole leaks in spite of the care with which they are made and assembled. Unless these defective elements are removed from the pile within a very few hours after the hole develops, the whole structure might be lost, he said.

The banquet was one feature of the three and one-half day program October 5-8. The technical program of 35 papers went smoothly. Some technical committee meetings were held as scheduled.

One of the three scheduled plant visits was cancelled but capacity crowds attended the visits to the Naval Research Laboratory and the Southern Galvanizing Company.

Total attendance was 301. This number included about 30 ladies.

Committee to Prepare
Regional Meeting Guide

Principal business at a meeting of Northeast Region's board of trustees at the Lord Baltimore Hotel October 4 was the naming of a committee to prepare a guide for planning and holding regional meetings. The committee, to consist of three men appointed by the chairman, will collect information on the operations and budgets for past meetings, correlate this information and prepare a guide which can be used by those conducting conferences in the future.

The board also discussed the problems associated with the Delaware Coatings Association, the division of membership areas between Wilmington and Philadelphia Sections, the work of section education committees and other matters.

Waynes W. Binger, Alcoa Research Laboratories, New Kensington, Pa., regional chairman, presided. Other officers also present were Frank E. Costanzo, regional director and A. F. Minor, regional vice chairman.

R. C. FRANCIS presents his paper "Service Test Experience With an Automatically Controlled Platinum Anode Cathodic Protection System of an Active Destroyer" during the Cathodic Protection Symposium at Baltimore.

FORMER MARYLAND GOVERNOR Theodore R. McKeldin (left) is shown conversing with some of the guests following the NACE Northeast Region banquet. He was toastmaster for the event.

NORTHEAST REGION guests are shown here at the oyster roast on the night of Monday, October 5. In the photograph at the left oysters and clams are being opened for eating. At the right some of the 160 or more present are shown enjoying their meal.

Interested in
Refinery Corrosion?

You will want to read (and keep for reference) three ASTM-ASME Joint Committee on Effect of Temperature on the Properties of Metals papers:

An Industrial Experience of Severe Metal Wastage Resulting From Burning Methane With Oxygen

Metal Deterioration in Atmospheres Containing Carbon-Monoxide and Hydrogen at Elevated Temperatures.

Corrosion in a Hydrocarbon Conversion System

These papers presented during Part 2 —Refinery Industry Symposium, NACE 15th Annual Conference at Chicago, March, 1959.

Scheduled for Publication in
DECEMBER CORROSION

Southeast Region News

Speakers Added to Florida Nov. 16-20 Short Course

Additional speakers have been added to the final program for the 4th Annual General Florida Conference 1959 Corrosion Short Course to be held November 16-20 at the Key Biscayne Hotel, Miami, Fla.

The short course program schedule was printed on page 76 of the October issue of CORROSION.

Speakers and their topics to be added are as follows:

Characteristics of Anodes for Impressed Current in Sea Water, by T. P.

SOUTHEAST REGION CONFERENCE held October 1-2 at the Robert Meyer Hotel in Jacksonville, Florida, heard NACE President Hugh P. Godard (top photo above) give the opening address on "What NACE Can Do For You." The center photo shows some of the 100 registrants and guests listening to presentation of a technical paper at one of the conference sessions. Bottom photo is W. R. Dana of Amercoat Corp., South Gate, Cal., presenting his paper on "Rigid Plastic Pipe."

May, International Nickel Co., Inc.

Pipe Type Cable, by D. E. Knauss, Florida Power Corp.

Vinyl Coatings, by D. R. Meserve, Metal & Thermit Corp.

Epoxy Coatings, by J. W. Cushing, Carboline Co.

•

East Tennessee Section has scheduled Frank L. LaQue as guest speaker for the November 18 joint meeting with ASM's Oak Ridge Chapter. Topic will be "Research in the Materials Field."

Norman Hackerman of the University of Texas spoke on metal dissolution and its retardation at the October 22 meeting.

•

Atlanta Section heard J. P. McArdle, Jr., of American Telephone & Telegraph Company speak on "A Distributed Anode Bed in an Urban Area" at the September 28 meeting.

Next section meeting is scheduled for November 23.

•

Birmingham Section December 4 meeting will feature a paper on recent rectifier developments, to be presented by John A. Waugaman of Good-All Electric Mfg. Co. The dinner meeting will be held at the Molton Hotel.

The September 21 meeting included a paper by James P. McArdle, Jr., of American Telephone and Telegraph Company on a distributed anode system in an urban area.

Attention Librarians

and others who bind CORROSION by Volumes!

The index to CORROSION's 1959 (Volume 15) issues will include alphabetical subject and author references to the articles published in the Technical Topics Section. The growing number and importance of these articles makes necessary to include them in the indexing.

•

Those who bind CORROSION by volumes and who customarily extract Technical Section pages are reminded that it will be desirable to extract also the Technical Topics Section and add it to the Technical Section of each issue. Although the Technical Topics Section does not have cumulative numbering of pages, it will be relatively easy to locate article if this procedure is followed.

NATIONAL and REGIONAL MEETINGS and SHORT COURSES

1960

January 17-20—Canadian Region Eastern Division. Toronto.

February 10-12—Canadian Region Western Division. Vancouver.

March 14-18—16th Annual Conference and 1960 Corrosion Show. Dallas, Texas. Memorial Auditorium.

Oct. 6-7—10th Annual Western Region Conference, Sheraton-Palace Hotel, San Francisco, Cal.

Oct. 6-8—Southeast Region Conference, Dinkler-Plaza Hotel, Atlanta, Ga.

Oct. 11-14—Northeast Region Conference. Prichard Hotel, Huntington, W. Va.

Oct. 19-20—North Central Region Conference. Schroeder Hotel, Milwaukee.

Oct. 25-28—South Central Region Conference, Mayo Hotel, Tulsa.

1961

March 13-17—17th Annual Conference and 1961 Corrosion Show, Buffalo, N. Y., Hotel Statler.

Oct. 9-11—North Central Region Conference, St. Louis, Chase Park Plaza Hotel.

Oct. 24-27—South Central Region Conference, Houston, Shamrock Hotel.

Oct. 30-Nov. 2—Northeast Region Conference, New York City, Hotel Statler.

Southeast Region Conference, Miami, Fla., in conjunction with Miami Section's short course.

1962

March 18-22—18th Annual Conference and 1962 Corrosion Show. Kansas City, Municipal Auditorium.

October 16-19—South Central Region Conference, Hilton Hotel, San Antonio, Texas.

Southeast Region Conference, Birmingham, Ala.

SHORT COURSES

1959

November 16-20—4th Annual General Florida Conference 1959 Corrosion Short Course. Key Biscayne Hotel, Miami.

December 7-11—University of Illinois Corrosion Control Short Course. Urbana Campus.

1960

January 28-29—5th Annual Houston Section 2-Day Course in Practical Corrosion Control Systems. Rice Hotel, Houston.

April 27-29—Portland Section Corrosion Control Short Course.

October 3-5—Corrosion Control Short Course, sponsored by Western Region and University of California.

•

NACE Certificates of Membership are available from the Central Office. Measuring 5½ x 8½ inches, the certificates cost $2 each and are signed by the association president and executive secretary.

•

Certificates for past chairmen of regions and sections, measuring 9 x 12 inches, are available from the Central Office at $7.50 each.

Western Region News

194 Attend Ninth Annual Western Region Conference

A total of 194 registered for the 9th Annual Western Region Conference held Sept. 29-Oct. 1 in Bakersfield, Cal.

Interest in the technical program remained high, even in the last scheduled meeting which was a forum on general corrosion problems. A panel of experts consisting of the conference symposia chairmen, with H. J. Keeling as moderator, led the discussion.

NACE Vice President George Best presented the conference keynote address on "New Horizons for NACE." F. S. Wilkes of Dearborn Chemical Company gave a luncheon address on the first day of the conference on the corrosion problems encountered in atomic reactors.

At the Fellowship Hour and Banquet, Colonel Frank H. Mears, base commander of Edwards Air Force Base, spoke on the Air Force Flight Test Center.

•

Western Region Conference for 1960 will be held October 6-7 at the Sheraton-Palace Hotel in San Francisco. This 10th Annual Conference will be preceded by a 3-day corrosion control short course on October 3-5 at a location to be selected by the University of California.

The following chairmen have been named to plan and arrange the 1960 conference: General Conference Chairman C. Jackson Puckett, Dow Chemical Co., Pittsburgh, Cal., Program Chairman William P. Simmons, Alloy Steel Products Co., Inc., San Francisco, and Publicity Chairman James B. Dotson, Pyromet Co., San Francisco.

•

Portland Section heard Otto Hudrlik, Ralph Mattison and Keene Shogren discuss corrosion fundamentals at the September 10 meeting. Nominations for the 1960 section officers were received for election at a later meeting.

SECTION CALENDAR

November

4 Central Oklahoma Section. Tropical Cafeteria. Oklahoma City.
5 West Kansas Section.
5 Pittsburgh Section. Coatings Roundtable Discussion by five speakers.
10 San Francisco Bay Area Section.
10 Montreal Section. New Plastics.
16 Baltimore-Washington Section. Problems, Testing and Mitigation Methods Peculiar to Corrosion Control of Lead Sheath Cables, by T. J. Maitland.
17 Chicago Section. Chicago Engineers Club. Cathodic Protection.
17 San Joaquin Section.
18 Los Angeles Section.
18 East Tennessee Section. Research in the Materials Field, by Frank L. LaQue.
19 Teche Section. Petroleum Club.
19 Detroit Section. Annual election. Uses of Polyester-Fiberglass in Chemical Industry, by W. A. Symanski, Hooker Chemical Corp.
20 Ohio Valley Section. Louisville YMCA.
23 Tulsa Section.
23 Atlanta Section.
24 East Texas Section. Longview Hotel in Longview.
24 Panhandle Section.
26 Edmonton Section. Corona Hotel.

December

1 Shreveport Section. Capt. Shreve Hotel. Plant Corrosion.
3 West Kansas Section.
3 Sabine-Neches Section
3 Pittsburgh Section. Underground Roundtable. Discussion by six speakers.
3 Teche Section. Petroleum Club.
4 Birmingham Section.
7 North Texas Section.
8 San Francisco Bay Area Section.
15 East Texas Section. Longview Hotel in Longview.
15 Philadelphia Section.
29 Panhandle Section.

Unwrapped, Uncoated Aluminum Pipe Used For 8-inch Gas Line

Aluminum pipe is being used without a coating or wrapping by Aluminum Company of America for a 4500-foot pipeline to be part of a gas gathering system at a Point Comfort, Texas, plant.

Alcoa's Unistrength pipe was used with thinner walls along the pipe length and heavier thickness at end to reduce weight and material cost, estimated at 20 percent by Alcoa.

A new automatic pipe welding machine designed and developed by Alcoa was used to join the 40-foot sections. The machine gives full penetration without the use of back-up rings and completes a pass on 8-inch pipe in 17 seconds, according to Alcoa.

This pipeline will carry dry gas at a 500 psi.

Other installations of aluminum pipe have been used through sand, gumbo and salt marshes in the Texas Gulf Coast area for over two years. Some of the first aluminum pipelines were laid 11 years ago.

NEW 8-INCH ALUMINUM PIPELINE installed by Aluminum Company of America at its Point Comfort, Texas, plant is shown being fed into an automatic welding machine. The pipeline will be buried without coating or wrapping as part of a gas gathering system.

Current Investigation Given On Stress Corrosion Cracking

Current investigation of stress corrosion in low carbon steel and the role of hydrogen in corrosion cracking are given in a progress report by Hugh L. Logan on the National Bureau of Standard's Project 4148 (Report No. 6471) on the mechanism of stress corrosion cracking of metals.

Investigation on Low Carbon Steel

The susceptibility of an aluminum killed low carbon (0.19 percent) steel to stress corrosion cracking in a boiling aqueous NH_4NO_3 solution has been studied. As given in an earlier report, considerable difficulty had been encountered in obtaining failures in conventional tensile specimens of this steel even at stresses above the yield strength. Hence the use of notched specimens was continued.

Specimens were machined from $\frac{1}{2}$-inch diameter stock with a 0.250-inch diameter at the root of the notch and a root radius of 0.005 inches. All specimens are insulated with plastic tape, except over the notched area, before they are placed in the 20 percent NH_4NO_3 solution.

Specimens were subjected to a stress just above that at which the true stress-true strain curve deviated from a straight line. Time-elongation and time-electrochemical solution potential data have been obtained for several specimens. The electrochemical solution potential changed from —0.70 volts (with respect to a saturated calomel electrode) to approxi-

mately —0.35 volts as the temperature of the corrodent was raised from 25 C to its boiling point, approximately 103.5 C.

After initial extension on loading, which may occur at a diminishing rate for as long as 30 minutes, extension becomes discontinuous with time. These extension changes were accompanied by momentary increases (in the negative direction) of the electrochemical solution potential.

Application of cathodic protection, after stress-corrosion cracks have developed, has prevented propagation of cracks for as long as 48 hours.

A set of silicon killed low carbon steel specimens (carbon content also 0.19 percent) has been machined to the same dimensions as the aluminum killed specimens described above. The true stress-true strain curves have been determined for these specimens. It is planned to compare the susceptibility of this steel to stress-corrosion cracking with that of the aluminum killed steel by determining the relative exposure periods to failure of the two steels.

Role of Hydrogen

Specimens of 4130 steel, heat treated to have a yield strength of approximately 150,000 psi, have been used in this investigation. The specimens, hollow cylinders connected to a vacuum system, were stressed to approximately 120,000 psi and exposed in 0.5 percent aqueous acetic acid solution that has been sat-

urated with H_2S. Specimens generally failed in 16 to 20 hours with most of the extension occurring in the last few minutes of the exposure period. Most of the failure has the characteristic appearance of shear fracture.

The rate of build up of pressure (due to hydrogen) in the interior of the specimen was determined periodically. Data obtained on one specimen indicated that little hydrogen diffused through the steel during the first 30 minutes of exposure. The diffusion rate then increased with increased exposure period. The most rapid change in rate occurred between the 30th and 90th minutes. Specimen temperature was approximately 30 C. Presence of hydrogen in the interior of the specimen was proved by mass spectrographic methods.

NBS Checks Measurement Accuracy by Gage Blocks

Using gage blocks, the U. S. National Bureau of Standards has certified the accuracy of its length measurements to better than one part in five million. Gage blocks, carefully made steel blocks, are used to monitor manufacturing processes in mass production of interchangeable machined parts. Extreme accuracy is required for some manufacturing. One manufacturer states that an error of a millionth of an inch in the bore-hole of a missile gyro can result in a complete miss during a moon shot. The gage blocks were compared with the measured, engraved standard bars of the Bureau by B. J. Page of the NBS length laboratory. Blocks were re-measured in terms of wave lengths of light by Arthur G. Strang of the Bureau's engineering metrology laboratory.

Permanent Magnet to Be Used as Pump To Move Liquid Sodium in AEC Reactor

A permanent magnet considered to be the world's largest is to be used to pump liquid sodium in a breeder reactor for the Atomic Energy Commission. This reactor will produce electrical power on the Argonne Idaho Division site at the National Reactor Testing Station near Idaho Falls, Idaho.

Made by Arnold Engineering Company, Marengo, Ill., the magnet is made of Alnico V material and weighs 1720 pounds. Over-all dimensions are 52½ by 36 by 10 inches with a gap length of 16½ inches and a gap volume of 1584 cubic inches. About 500,000 ampere turns were needed to magnetize the unit.

Electromagnets are generally used to pump liquid sodium in this atomic energy application, but a large permanent magnet was required in the Idaho application because the magnet will be surrounded by liquid metal.

Sodium used in the reactor acts as a heat transfer medium or coolant in much the same way as water can be used, but sodium is more effective. Heat is absorbed within the reactor and is pumped outside to heat water in a heat exchanger or boiler.

The large magnet will help pump the highly radioactive sodium at elevated temperatures by interaction between a current passing through the sodium at right angles to a strong magnetic field. This produces a force in the sodium when directed through a closed piping system serving as a continuous supply of liquid sodium.

ASHRAE to Meet Feb. 1-4

The semi-annual meeting of the American Society of Heating, Refrigerating and Air Conditioning Engineers, Inc., will be held in Dallas, Feb. 1-4, 1960. The second Southwest Heating and Air-Conditioning Exposition will be held concurrently with the meeting. Meeting headquarters will be the Baker Hotel. The Exposition will be in Memorial Auditorium.

BOOK NEWS

Writing and Publishing Your Technical Book. 50 pages, 6 x 9 inches, paper. F. W. Dodge Corporation, 119 West 40th St., New York 18, N. Y. Available free on request.

Designed to help authors through the initial stages of developing technical book manuscripts, it describes how to prepare manuscripts of business, industrial, engineering and professional books and how to arrange for their publication.

Illustrations for Publication and Projection. 14 pages, 8½ x 11 inches, paper. American Society of Mechanical Engineers, 29 West 39th St., New York 18, N. Y.

Provides easy-to-use standardized procedures to save an author's time and expense in preparing illustrations for publication or projection.

Basic Mechanical Engineering (PB 151693). Chief of Civil Engineers, Bureau of Yards and Docks, U. S. Navy. 106 pages. Available from Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. Per copy, $2.50.

Describes design and installation of plumbing, heating, ventilating, air conditioning and dehumidifying systems and elevator systems in Navy shore facilities.

Corrosion Prevention (PB 151756). Office of the Chief of Civil Engineers, Bureau of Yards and Docks, U. S. Navy. 431 pages. Available from Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. Per copy $6.

Prepared for personnel engaged in construction, operation and maintenance of naval shore facilities, the book gives data on atmospheric, submerged and subsurface corrosion and corrosion on areas alternately wet and dry. Describes methods and materials the Navy has found to be most practicable in controlling or minimizing corrosion. Also discusses corrosion processes caused by use of dissimilar metals with emphasis on electromotive force series and galvanic corrosion, direct chemical attack, stray currents, microbiological and atmospheric attack and marine corrosion.

Atmospheric Exposure of Wrought and Cast Aluminum Alloys. 100 pages. Reprints from ASTM Proceedings. Available from American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa. Per copy, $1.75.

Gives data on exposure at Freeport, Texas, of plan and riveted panels, tension bars, etc. Data show that from the mechanical strength point of view, properly selected magnesium or aluminum alloys do not necessarily need costly supplementary finishes to serve as corrosion protection in some environments. Shows that all aluminum and magnesium alloys do not deteriorate rapidly in severe marine exposures.

•

More than 20,000 cards have been issued by the NACE Abstract Punch Card Service.

•

7464 copies of NACE Technical Committee Reports published in CORROSION were sold in 1958.

PERIODICALS

Soviet Physics—Crystallography. Bimonthly. In English. Translation Journals, American Institute of Physics, 335 East 45th St., New York 17, N. Y. Annual subscription in U. S. and Canada: $25; $27 elsewhere. Special subscription to libraries of non-profit academic institutions: $10 in U. S. and Canada; $12 elsewhere.

This translation of the USSR Academy of Sciences publication offers experimental and theoretical papers on crystal structure and morphology, lattice theory, diffraction studies and other topics of interest to metallurgists. Subscriptions are being accepted to the second volume, which are translations of issue published during 1958 in the USSR. Limited numbers of the six 1957 issues are available also.

Corrosion Reporter. Quarterly. Vol. 6, No. 1, July, 1959. 15 pages. International Nickel Co., Inc., 67 Wall St., New York 5, N. Y.

Revival of Inco's publication that is devoted to discussions of current corrosion problems. The July, 1959, issue is in two parts: materials for missiles and other space vehicles and corrosion problems encountered with fuels and oxidizers. Editor of the publication is W. D. Mogerman.

Pakistan Journal of Scientific and Industrial Research. Monthly. In English. Vol. 2, No. 1, January, 1959. Pakistan Council of Scientific and Industrial Research, 141-S/2, PECHS, Karachi 29, Pakistan. Annual subscription: Rs. 15/-post free. Single copies: Rs. 4/-post free.

British Demonstrate Use Of Plastics in Aircraft

Use of plastics by the British in the manufacture of aircraft was demonstrated at the exhibition of the Society of British Aircraft Constructors held during the flying display at Farnborough, England this year.

Main trend in plastics was the evaluation and improvement of manufacturing technique of resin-glass structures. One item on display was a filament-wound glass fibre radome. The process makes it possible to produce shapes and forms difficult or impossible to produce by other methods. Radomes 5 feet in diameter and 15 feet long with tensile strengths from 150,000 to 160,000 psi are made by the process.

Non-Destructive Testing Courses Are Offered

Training courses in non-destructive testing are conducted regularly by Magnaflux Corporation at their Chicago, Ill., plant. Sessions cover the basics, theory and practice of non-destructive testing.

Supervisors of quality control, inspectors, operators and persons responsible for personnel training have attended. Each week-long class is limited to eight men. Time is divided equally between laboratory inspection, class discussion and lectures.

Additional information can be obtained from Magnaflux Corp., 7300 West Lawrence Ave., Chicago 31, Ill. Course fee is $100.

Coal-Tar Enamel Coatings Protect Pipe for 20 Years

Coal-tar enamel coatings on a 30-inch water line in Tacoma, Wash., 20 years ago have remained in perfect condition, making the pipe re-usable without further coating, according to the city's water division superintendent.

A 365-foot section of the line had to be removed to make way for a freeway. Examinations showed the pipe to be in good condition. The original coating had to be repaired only at the places damaged during removal.

When first installed in 1939, the pipe was given a 3/32-inch spun coat of coal-tar enamel on the inside. Pipe exterior was given alternate layers of coal-tar enamel and asbestos felt to a total thickness of 7/32-inch.

Ceramic Chamber Built

A ceramic chamber is being built to contain a thermonuclear reaction which may produce a temperature above 100,-000,000 degrees Centigrade. The chamber will be the heart of the C Stellarator. This machine is designed to keep the H-Bomb reaction suspended in a powerful magnetic field within a tube incorporating the alumina-ceramic chamber. If the process is successful, cheap abundant electric power will result. Aluminum Company of America is supplying the alumina used as a raw material in making the ceramic chamber.

Solid Fuel Conference

Joint conference on solid fuels was held October 27-29 in Cincinnati, Ohio, by AIME and ASME. A paper on fireside corrosion of superheater and reheater tubing was included on the technical program.

British Spend 1½ Billion To Control Corrosion

British industry annually spends over 1½ billion dollars on corrosion control, according to the Leonard Hill Technical Group in London. The British Corrosion Exhibition to be held Nov. 29-Dec. 2, will be almost twice the size of the 1959 show, its sponsors say. Similar to NACE's annual Corrosion Show, the British will display anti-corrosion materials and methods.

•

Over 20,000 cards have been issued by the NACE Abstract Punch Card Service.

NEW PRODUCTS

Equipment Services   **Materials Literature**

Aluminum

Aluminum Pipeline will be installed for Superior Oil Company in Lake Maracaibo, Venezuela, as suction line for fire protection pumps. The 16-inch underwater line will be fabricated by Graver Tank Corp., East Chicago, Ind., and Reynolds Metals Company will supply the aluminum alloy. The 1800-foot pipe was designed by Pipeline Technologists, Inc., Houston, Texas. Aluminum was chosen, according to Superior Oil corrosion engineers, because its corrosion resistance permits installation in the lake without protective coating or wrapping.

Automobile Wheels with integral hub and brake drum made of aluminum will be optional equipment on some 1960 models. Prototype models of the integral wheel developed by Kaiser Aluminum, 1924 Broadway, Oakland 12, Cal., were tested in 1955 and 1956.

Aluminum Sheet from Alloy 5456, a weldable aluminum-magnesium alloy series, is being produced by Aluminum Company of America, Alcoa Bldg., Pittsburgh 19, Pa., in rolled thicknesses from 0.051 to 2.00 inches for use in missiles, ships, trucks, storage tanks and structural applications.

Abrasives

Abrasive Wheel Recommendations for grinding are listed in a new Specifications Catalog available from Carborundum Co., Niagara Falls, N. Y. Material, work and operation with recommendations on abrasive, grit, grade and bond are given.

Porcelain Enameling Process said to be adaptable to existing plant facilities is being introduced by Chas. Pfizer & Co., Inc., 800 Second Ave., New York 17, N.Y. Known as the Ray-Davis Process, it uses citric acid in the pickle bath instead of sulfuric acid.

Coatings—Inorganic

Zinkote, a new zinc coating developed by Amercoat Corp., 4809 Firestone Blvd., South Gate, Cal., is claimed to be self-curing without separate curing solution. It is applied over bare steel by brush, spray or roller. According to the manufacturer, the coating gives protection to steel surfaces exposed to water, severe weathering, salt spray and abrasion.

E & M Equipment Company, 2415 15th St., Denver, Colo., will be the Rocky Mountain representative of Ceilcote Company and its line of industrial corrosion control materials.

Turcoat Low Temp, a phosphating compound developed by Turco Products, Inc., 24600 South Main St., Wilmington, Cal., is claimed to operate at a temperature 75 degrees lower than that required by conventional phosphating processes.

Coatings—Organic

Geon Vinyl, a product of B. F. Goodrich Chemical Co., 3135 Euclid Ave., Cleveland 15, Ohio, is being used by steel producers as a finish on steel sheet in place of a baked enamel. Used by furniture and appliance manufacturers, the vinyl coated steel gives a durable, furniture-like finish, according to B. F. Goodrich.

Pyralux, a new Du Pont fluorescent enamel for safety marking and advertising painting of commercial vehicles, is described in a folder available from Finishes Division, Du Pont Company, Wilmington 98, Del.

New Chart entitled "Comparison of Maintenance Coating Systems" designed for engineers and maintenance personnel is available from Carboline Co., 32 Hanley Industrial Court, Brentwood 17, Missouri. The chart compares 17 standard systems, showing the strong and weak points of each. Resistance ratings are listed for acid, alkali, solvent, water, weathering, flexiblility, impact and abrasion and temperature conditions.

Del-Coat, a polyurethane liquid resin developed by Delka Research Corp., 1333 E. L. Grant Highway, Bronx 52, N. Y., is designed for application over old roofs for sealing and revitalizing asphalt shingles. The formulation is brushed on and followed by a layer of sifted sand.

Stripper S-28, second in a series of chlorinated strippers for epoxy enamels which can be diluted with water, according to the manufacturer, has been introduced by Enthone, Inc., New Haven, Conn., subsidiary of American Smelting and Refining Co. The new product is claimed to strip synthetic enamels rapidly at room temperature and at dilutions as high as 1 part stripper to 20 parts water.

Instruments

Ultrasonic Pickling of steel bar stock has been developed by Branson Ultrasonic Corp., 40 Brown House Road, Stamford, Conn. The new system is claimed to give uniformly clean stock in less time than the batch-dip system.

Automatic Recording Vacuum Balance is being produced by Wm. Ainsworth and Sons, Inc., 2151 Lawrence St., Denver, Colo. The balance weighs samples in air or inert gases, at atmospheric or reduced pressures, at room temperatures or elevated temperature and on the balance pan or suspended below the balance, according to the manufacturer.

Cleanliness Tester Model CM-1 is being manufactured by Branson Ultrasonic Corp., 40 Brown House Rd., Stamford, Conn. Developed by Graham Research Laboratories of Jones & Laughlin Steel Corp., Pittsburgh, Pa., the tester assigns numerical values to surface cleanliness where non-bonded soils are involved. According to the manufacturer, the tester measures smut residue after pickling of steel and evaluates detergents and oils used on cold mills, annealing performance and efficiency of electrolytic and alkaline cleaning lines.

Hi Volume Air Sampler, an air monitoring device available from Staplex Co., 777 Fifth Ave., Brooklyn 32, N.Y., was designed for detection of radioactive particles, smoke and smog and detection of mine and factory hazards.

Dual-Sensitivity D-C Voltmeter for measuring open circuit structure-to-soil voltages is described in Bulletin 1-3 available from Associated Research, Inc., 3777 W. Belmont Ave., Chicago 18, Ill.

Mergers

Turco-Wilkings ChemPlastics, Inc., has been formed by Turco Products, Inc., 24600 South Main St., Wilmington, Cal., and Wilkings Plastics Co., Inc. Activities will include manufacture of Fiberglas laminations, casting of epoxy resins and precision machining and assembling of plastic materials.

Atlas Mineral Products Co., Mertztown, Pa., subsidiary of Electric Storage Battery Co., 2 Penn Center Plaza, Philadelphia 1, Pa., has purchased controlling interests in Chemical Linings, Inc., Watertown, N.Y. The lining company designs, fabricates and installs corrosion resistant linings, tanks and towers for process industries.

Metals—Ferrous

Wrought Iron Piping used to carry brine for freezing an ice rink floor was recently removed because of concrete and structural failures. According to Chicago stadium officials, the wrought iron piping was in good condition after 24 years' service. About 53,000 feet of wrought iron pipe was used in the floor repair job, supplied by A. M. Byers Co., Clark Bldg., Pittsburgh 22, Pa.

Casting Alloys Booklet, available from International Nickel Co., Inc., 67 Wall St., New York 5, N.Y., contains data on range of properties, industries served and general applications for nickel-containing casting alloys.

Mill Shapes

Polypenco polycarbonate mill shapes are described in Bulletin BR-12, available from Polymer Corporation of Pennsylvania, Reading, Pa. Included are a physical property chart, chemical resistance table and suggested applications for polycarbonate rod, plate, discs and tubing.

New Plants

Dow Corning Corporation will build a new technical service and development laboratory adjacent to its other plants in Greensboro, N. C., to study problems in the textile, paper and brick industries.

Sohio Chemical Company is building a new acrylonitrile plant at Lima, Ohio, which will use a direct conversion of refinery propylene and anhydrous ammonia in the manufacture of acrylonitrile.

Reynolds Metals Company has begun production of its Reynolon polyvinyl chloride and polyvinyl alcohol films at its Grottoes, Va., plant.

Plastics

Chemore Corporation, 21 West St., New York 6, N.Y., will be general representative for Moplen plastics and chemicals manufactured by Montecatini of Milano, Italy.

Baker PL-11, an acrylic polymer developed by J. T. Baker Chemical Co., Phillipsburg, N.J., is described in a technical brochure available from the company. The polymer is a thermoplastic resin said to be suitable for injection molding and extrusion.

NEW PRODUCTS

(Continued From Page 92)

Atlac 382, a polyester resin developed by Atlas Powder Company's Chemicals Division, Wilmington 99, Del., is described in two new bulletins available from the company. Properties, applications and room-temperature curing system are given.

•

Tetra-Etch, an activated form of sodium in solution, is a new method of bonding polytetrafluoroethylene to itself and to other materials. The new bonding material was developed by W. L. Gore and

Associates, Inc., 487 Papermill Road, Newark, Del.

•

Intricate Shapes in extruded polytetrafluoroethylene are being produced to specifications by Pennsylvania Fluorocarbon Co., Philadelphia, Pa. Shapes include insulators, spacers, supporting channels or ductwork for electrical circuits and terminal receptacles or plugs.

•

Rigid PVC Pipe is being manufactured by a new plastics division of Glamorgan Pipe & Foundry Co., Lynchburg, Va., Additional information can be obtained from the Plastics Division Office of the company, 116 John St., New York 38, N.Y.

•

Amer-Plate, a polyvinyl chloride sheet for lining plating, pickling and other tanks and vessels, is described in a brochure available from Amercoat Corp., 4809 Firestone Blvd., South Gate, Cal.

•

Rigivin Solid Plastic Fan, designed to exhaust corrosive and poisonous fumes, is being produced by Heil Process Equipment Corp., 12901 Elmwod Ave., Cleveland 11, Ohio. All parts in contact with fumes are constructed of unplasticized polyvinyl chloride.

•

PVC Utility Blowers, constructed of unplasticized rigid polyvinyl chloride, are being produced by Industrial Plastic Fabricators, Inc., Endicott St., Norwood, Mass. The direct drive blowers are designed for use in laboratories where corrosive fumes or moisture are a problem.

Pumps

Johnston Engineering Sales Co., P. O. Box 232, Wayland, Mass., has been ap-

pointed a distributor of Ampco centrifugal pumps, manufactured by Ampco Metal, Inc., 1745 South 38th St., Wilwaukee 46, Wisconsin.

•

Turbocraft Series 3000 Pump, a new close-coupled petrochemical and cryogenic transfer pump, is described in a catalog sheet available from Turbocraft, Inc., 492 E. Union St., Pasadena, Cal.

•

Gearchem Pumps, manufactured by Ec Engineering Co., 12 New York Ave, Newark, N.J., are being produced in electrolytically pure nickel to prevent iron contamination of bromine and caustics according to the manufacturer, to permit pumping water-thin, non-lubricating fluids without seizing or excessive wear.

•

Model D Golden Thief, a new vacuum pump available in stainless steel and aluminum manufactured by W & W Manufacturing Co., P. O. Box 9311, Chicago 90, Ill., is designed for sampling where contamination must be avoided and where corrosive liquids are involved.

•

Mechanical Seal Failure on pump shafts in water systems is described in Technical Bulletin 591 available from Water Service Laboratories, Inc., 615 West 131st St., New York 27, N.Y. Common causes of failure, relation of abrasive action to seal longevity and importance of proper alignment of pump and drive shaft are discussed.

Solvents

New Industrial Solvent for cleaning and rust control is described in a folder available from Frank A. Hoppe, Inc., 2314 North 8th St., Philadelphia 33, Pa. Based on a gun cleaning solvent, the new cleaner is applied by brush and is said to keep metals rust-free and will not stain wool, cotton, silk, rayon, nylon or other synthetic yarns.

•

Freon Solvents, produced by Du Pont de Nemours & Co., Wilmington, Del., for removal of dirt and grease are nonflammable and virtually nontoxic yet safe enough for use on delicate gyroscopes and precision instruments, according to Du Pont. The solvents are chemically related to fluorinated hydrocarbon compounds used as refrigerants and aerosol propellents.

Tapes

Warco Laminated Tape, a vinyl and butyl laminated pipe wrapping tape developed by West American Rubber Co., 410 North Ave. 19, Los Angeles, Cal., has a heavy mastic layer of butyl with an outer cover of vinyl. According to the manufacturer, the tapes are designed to give resistance to abrasion and punctures from backfilling.

•

Scotch Brand Paklon, a transparent film-backed tape for packaging applications manufactured by Minnesota Mining and Manufacturing Co., St. Paul 6, Minn., is designed to resist water, acids, alkalies, other strong solvents and wide temperature ranges.

•

Pipeline Coating Package including pressure-sensitive polyethylene tape and an overwrap has been introduced by the new Corr-Prev Division of Chase & Sons, Inc., North Quincy, Mass.

Titanium and Tantalum

Titanium-Clad Vessels are being fabricated by Chicago Bridge & Iron Com-

NEW PRODUCTS

(Continued From Page 94)

pany at its Birmingham, Ala., plant. The vessels are designed for use in the chemical, petrochemical, paper and other processing industries.

New Titanium Alloy has been developed
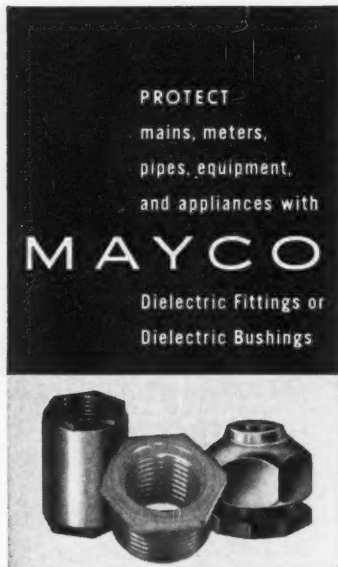
in the Research Division of New York University's College of Engineering. Claimed to be superior in strength, ductility and toughness to comparable alloys, the new product is composed of 6 percent aluminum, 6 percent vanadium, 2 percent tin, 0.5 percent iron, 0.25 percent copper and 85.25 percent titanium. Components fabricated from the new alloy, according to the research staff, will weigh from 20 to 40 percent less than those fabricated from high-strength steels.

•

Titanium Order for 28,000 pounds was supplied by Republic Steel Corporation for use in Freeport Nickel Company's new nickel extraction plant at Moa Bay, Cuba. Titanium was used in the plant for draft tubes, valves, piping, internals and nozzle linings to resist the corrosive and eroding slurries of cobalt, nickel and sulfuric acid at elevated temperatures and pressures.

•

Tantalum Tubing is being produced in thin walled, butt-welded form by Haynes Stellite Company, 420 Lexington Ave., New York 17, N.Y., a division of Union Carbide Corporation.

Tubing

Columbium, Tantalum and Vanadium tubing analyses are given in Special Analysis Memo No. 121 available from Superior Tube Co., 1714 Germantown Ave., Norristown, Pa. The memo gives general information and applications for the three analyses. Physical, mechanical and fabricating properties are included.

•

Tubing Cost Folder entitled "How to Cut Cost by Using Alloy Mechanical Tubing" is available from Tubular Products Division, Babcock & Wilcox Co., Beaver Falls, Pa. Folder discusses initial cost, structural advantages of tubing, fabrication by machining, types of steel, types of tubes and procurement tips.

Valves

Lonergan Valves and Gauges, manufactured by J. E. Lonergan Company, 211 Race St., Philadelphia 6, Pa., will be

distributed in the St. Louis area by Industrial Process Equipment Co., 4903 Delmar, St. Louis, Mo.

•

Tru-Lift FP-8 Pump Valves, designed primarily for low pressure corrosive service, are being produced by Dixell Development and Manufacturing Co., 1810 Ojeman, Houston, Texas. Applications recommended by the manufacturer include low pressure water flooding, sour crude gathering lines, acrid transfer pumps, paraffin crude lines, fuel transfer systems and other services where large volumes of fluids are handled.

•

Gear-Vac Valves designed for handling viscous media are being produced by Eco Engineering Co., 12 New York Ave., Newark 1, N. J. Heavy greases, viscous and tacky plastisols, encapsulating compounds, heavy creams, gels sealing compounds and plasticizers are among the media which the manufacturer claims can be handled by the valves.

Welding

Steel Welding Handbook is available from United States Steel, 2 William Penn Place, Pittsburgh 30, Pa. Entitled "How to Weld U.S. Steel's T-1 Steel," the booklet includes a heat input calculator to determine correct heat amounts as related to amps, volts and speed of the welding arc.

MEN in the NEWS

D. B. Coyle has been appointed sales representative of Midwestern Pipe Line Products Co. He will make his headquarters at the home office of the Tulsa firm.

•

Gerald E. McDermott has been named chief estimator and head of material sales for Corrosion Rectifying Co., 5310 Ashbrook, Houston 36, Texas.

•

Ray F. Trapp, NACE member, has formed a new Company (Pipeguard Corporation with headquarters at 3131 Piedmont Road, N.E., Atlanta 5, Ga.) to furnish corrosion materials to the gas industry.

•

Carleton C. Long, NACE member affiliated with St. Joseph Lead Co., Monaca, Pa., has been elected president of The Metallurgical Society of the American Institute of Mining, Metallurgical and Petroleum Engineers. **J. S. Smart, Jr.,** of American Smelting and Refining Co., New York City, has been named vice president of the society.

•

John P. Fraser, NACE member, has assumed duties as corrosion supervisor at Shell Pipe Line Corporation's Technical Development Laboratory in Houston, Texas.

•

A. W. Peabody, NACE member, has been appointed supervising engineer of the corrosion engineering group at Ebasco Services Incorporated, 2 Rector St., New York 6, N. Y.

•

Ellis D. Verink, Jr., NACE member, has been named manager of chemical and petroleum industry aluminum sales

MEN in the NEWS

(Continued From Page 96)

for Aluminum Company of America, Pittsburgh 19, Pa.

•

Jack N. Grossett, NACE member, has been promoted to manager of cold applied coatings sales in the tar products division of Koppers Company, Inc., Pittsburgh 19, Pa.

•

Richard D. Hobbs, NACE member, has been appointed sales and service specialist for the Safe-T-Clad, polyethylene tape division of Seamless Rubber Co., New Haven, Conn.

•

Edward D. Hinkel, Jr., has been appointed assistant sales metallurgist for Carpenter Steel Co., Reading, Pa.

•

Gerald Lewis has been appointed director of product engineering for Cooper Alloy Corporation, Hillside, N. J.

•

F. A. Redman has been appointed to the newly created position of special projects engineer for Harco Corporation, 4600 East 71st St., Cleveland 25, Ohio.

•

Walter K. Boyd, NACE member and assistant chief of the corrosion research division at Battelle Memorial Institute, presented a technical paper on the use of titanium in the pulp and paper industry at the 14th annual Engineering Conference of the Technical Association of the Pulp and Paper Industry last month in Pittsburgh, Pa.

•

Warren E. Berry, corrosion research specialist at Battelle Memorial Institute and a NACE member, presented a technical paper on corrosion resistant materials of interest to nuclear technologists at the International Conference on Aqueous Corrosion of Reactor Materials in Brussels, Belgium, October 13.

•

Richard P. Bell has been appointed general manager of paint sales for the merchandising division of Pittsburgh Plate Glass Co., 632 Fort Duquesne Blvd., Pittsburgh 22, Pa.

•

Guy J. Berghoff has been named president in charge of Pittsburgh Plate Glass Company's paint division in Pittsburgh 22, Pa.

•

David G. Braithwaite has been named executive vice president in charge of manufacturing, research and development for Nalco Chemical Co., 6216 West 66th Place, Chicago 38, Ill.

•

A. William Capone has been named manager of planning and development at the international division of Koppers Company, Inc., Pittsburgh 19, Pa. **F. M. Gibboney** was appointed controller of the division.

•

Walter Crafts, associate director of technology at Union Carbide Metals Co., Niagara Falls, N. Y., has been named president of the American Society for Metals.

•

Lester B. Cundiff has been named senior process engineer in the polyolefin department of American Viscose Corporation's Research and Development Division, 1617 Pennsylvania Blvd., Philadelphia 3, Pa.

TECHNICAL TOPICS

Accumulated Residues Attack

Chemical Distilling Column*

Abstract

Briefly discusses industrial problems in industry caused by residues and deposits. Presents data on distilling column in a chemical plant which was severely affected by accumulated residue, causing excessive downtime and maintenance. Concludes with suggestions to carefully analyze design and material selection in pilot tests.　　　　7.6.8

ACCUMULATIVE RESIDUES and deposits in the chemical industry are causing profit losses from downtime and heavy maintenance. Reboilers, distillation columns, accessories in vessels, lines, pumps and other chemical equipment are attacked by these residues.

Residues and deposits have been classified as inorganic, organic and combination organic-inorganic.[1] Industrial problems caused by these residues include scaling, plugging, corrosion, erosion, velocity changes, heat transfer effects, product contamination, distillation ratio changes, catalyst damage, odor or gas formation, product stability and hot spots.

An example of what accumulated residues can do in a large distilling column is shown in Figure 1. Residues from low and high flash point distillates plugged this 32-foot fractionating column made of cast iron. It had 98 bubble caps on each of the 42 bubble cap trays. Residues had affected the column's efficiency and resulted in considerable downtime. Several cleaning jobs were performed to remove deposits from internal accessories. Maintenance costs were three times the initial cost

★ Extracted from a paper titled "Accumulative Residues—Their Relation to Material Selection and Equipment" by H. Gilman, General Aniline and Film Corp., Dyestuff and Chemical Division, Linden, N. J., presented at the 15th Annual Conference, National Association of Corrosion Engineers, March 16-20, 1959, Chicago, Ill.

of the column, not including the loss due to inferior efficiency operation and downtime. The column was dismantled twice to remove the deposits.

In the upper trays of the column, expansion of the corrosion products split about half the bubble caps. Slots at the bottom of the bubble caps were plugged with residue.

The caps were piled on sheet metal and heated to about 800 F with a torch and left to cool. Comparison of caps before and after cleaning is shown in Figure 2. Figure 3 shows one plate reassembled after cleaning.

This column was used intermittently for short continuous cycles of distillation. Had it been a continuous production column, downtime due to maintenance cleaning would have been too serious and costly to continue using the equipment.

Corrosion engineers can reduce failures and delays caused by accumulated residues by programming additional material testing for residues and their origin. In many cases, a change in material prior to design and fabrication will eliminate the problem or at least minimize the amount of maintenance.

Conclusions

Accumulated residues should be carefully checked prior to material selec-

tion, particularly when the equipment is to be in continual production. The most conclusive data are obtained by exposing various specimens in continued pilot runs rather than in laboratory batch tests. If continuous pilot runs are not feasible, any presence of a coating or residue from laboratory or short field tests should be studied carefully and its accumulated effect considered.

References

1. C. M. Loucks and C. H. Groom. Chemical Cleaning of Heat Exchange Equipment. (Reprinted from ASME, October, 1949).
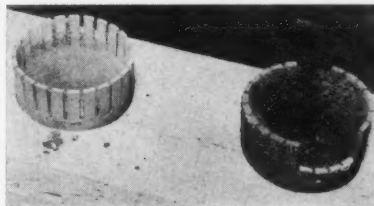
Figure 2—Bubble cap before (right) and after (left) flame cleaning. Caps were piled on sheet metal and heated to 800 F with a torch and left to cool. The deposits remaining in the cleaned cap on the left probably would have been removed also if an air stream had been played on the caps while hot.
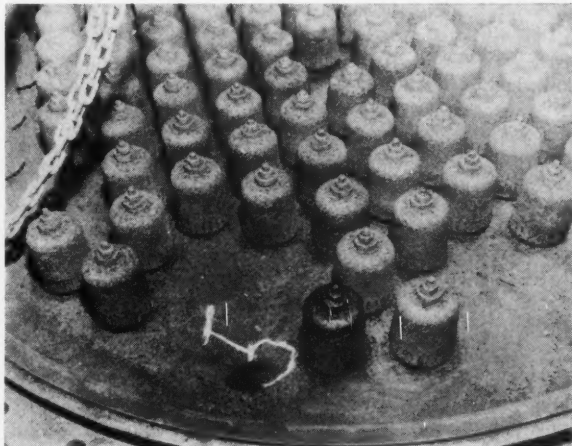
Figure 1—One of 42 bubble cap trays in a distillation column attacked by accumulated residues. The slots on the cap bottoms were plugged, but the chimneys were free.

Figure 3—Distillation column plate re-assembled after cleaning. The column was used immediately for short cycles of distillation.

Can Corrosion Problems*

Introduction

CAN CORROSION problems have existed ever since Bryan Donkin founded the can industry by introducing the tinned can as a container for foods. Much progress has been made in the technical aspects of packaging since the early years of canning, yet the criterion for successful packaging is essentially the same today: that the canned product must remain in a wholesome condition for the normal expected shelf life of the particular product. Normal shelf life expectancy is established by can supplier and packer through pack tests and commercial experience. As progress is made in packaging a particular product, the performance factor which limits shelf life often changes. For example, the limiting performance factor for soft drink product shelf life changed from perforation failure in the early stages of development of a tinplate package to iron pick-up tolerance in today's package.

An estimated two thousand products are packaged successfully in metal containers. Containers for this wide variety of products must satisfy a number of internal corrosion requirements. The effective corrosivity of any particular product may vary due to natural or formulation causes and those related to the canning operation.

The canning industry, particularly in the food field, is a highly competitive industry in which small cost variations can be a major factor. The best container from a technical viewpoint is of necessity a compromise to successfully meet all requirements. Further compromise is often necessary to satisfy the important requirement that the container be the soundest economic choice.

With all these requirements to meet, it is indeed surprising that one basic material, Donkin's tin coated steel modified by changes in the base steel composition, in thickness of tin coating and with additions of organic coatings still fills the role almost universally. Other container materials such as chemically treated steel (CTS), black plate, terne plate and aluminum are used in certain applications. In this article, consideration will be given only to corrosion problems with tinplate.

External corrosion is governed in general by the same factors responsible for the atmospheric corrosion of metals. Internal corrosion of cans, however, differs because practically no air or at least only limited air is present. How these factors and others influence the corrosion problems will be explained by discussing problem areas, controlling factors and means of control.

Types of Corrosion

Internal

Perforations are pin holes through the container metal caused by localized corrosion of iron (Figure 1). These failures are to be avoided because not only

★ Revision of a paper titled "Can Corrosion problems" by J. J. Daly, Jr. Continental Can Co., Chicago, Illinois, presented at a meeting of the Western Region Conference, National Association of Corrosion Engineers, Nov. 17-20, 1958, Los Angeles, California.
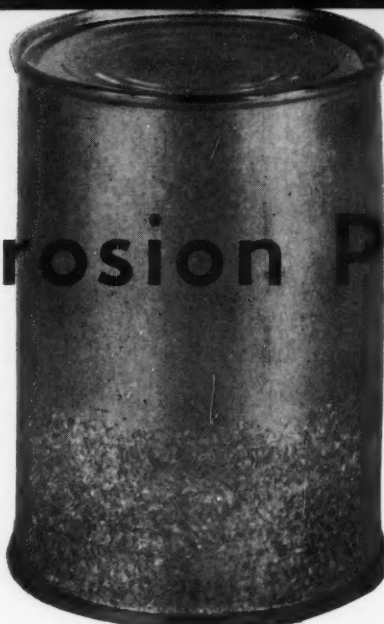
Figure 9—Non-uniform detinning on plain tinplate can.

Abstract

Describes various types of internal and external can corrosion normally encountered and their effects on the technical adequacy of the container and on consumer acceptance. Methods presented for corrosion control are product modification, container materials selection, packaging methods, storage conditions, protective coatings and chemical treatments. 7.5.2

is the individual can lost but also secondary spoilage of other cans is possible through exterior corrosion by the spilled product.

Springers or hydrogen swells are evidenced by a bulging of the can ends caused by hydrogen gas formation (Figure 2). Although the product may be satisfactory, springers are unacceptable because product spoilage is usually associated with the same external appearance. Hydrogen swells often are accompanied by excessive detinning in a plain can and certainly by high iron solution in a plain or organic-coated can.

Internal detinning is dissolution of tin from the tin plate surface. Although usually associated with plain tin plate, detinning can occur through enamel films (Figure 3). A reaction resulting in general over-all etching of the tinned surface is expected with some products and is acceptable; however, localized detinned areas where black appearing base metal is exposed may not be acceptable. Product bleaching or color loss usually accompanies detinning, and certain flavor changes may also occur. These changes are desirable for some products but not for others.

Internal rusting is the formation of loosely adhering, reddish-brown ferric oxide corrosion product on the corrosion site (Figure 4). Rust formation requires an excess of oxygen and thus when present in a can is usually found in the headspace area. Corrosion will continue under the rust layer; if sufficient corrosion capacity is available, perforation will result. Rust in itself is unsightly and may contaminate the product.

Enamel lifting is detachment of the organic film from the plate surface (Figure 5). Bubbles or loose flaps of film may be formed. Film detachment usually is accompanied by mild corrosion at the area of detachment; base metal may be exposed resulting in increased corrosion. The possibility that

particles of organic coating may drop into and contaminate the product is always present when lifting occurs.

Internal staining is adherent gray-black tin sulfide formation on the plate surface and occurs under organic films and on plain tinplate (Figure 6). Dark tin sulfide deposits appear about the same as base metal exposed through detinning and are just as objectionable.

Discoloration or formation of loose black iron sulfide (Figure 7) which occurs in the headspace is the reaction product of exposed iron and hydrogen sulfide. When it forms on an organic coated surface, it forms on the surface of the organic coating but not at the plate—organic coating interface. Formation of large quantities of iron sulfide usually results in black deposits on the product because the deposits are very loose.

External

External rusting is formation of loosely adhering reddish-brown ferric oxide (Fe_2O_3) at pores in the tin coating (Figure 8). Rusting may occur during processing because of corrosive water conditions, during storage because of poor warehouse conditions or during shipment because of poor transportation facilities. Perforations due to exterior corrosion are unlikely even with the thinnest tin coated plates, but rusty appearance of the cans, especially rust spotting through paper labels, is very objectionable.

External detinning, dissolution of tin from the tinplate surface, can result in localized base steel exposure or in a general over-all surface etching depending on severity of the reaction and cause of attack (Figure 9). Detinning can be caused by alkaline retort water or alkaline rinse water and by rusty equipment in electrochemical contact with cans. Appearance of the can may be readily degraded further because corroded areas are more susceptible to subsequent attack.

External staining is formation of any surface change other than detinning or rusting which interferes with normal bright appearance of the tin surface. This type staining is shown in Figure 10.

Internal Corrosion Control Measures

Product

Control of product corrosiveness is difficult because corrosiveness not only among products but within classes of products and at times in different lots of the same product. Formulated products are found more conforming in their corrosive characteristics than natural products which vary not only from growing area to growing area, but also from season to season. Pack test determinations, the industry's time honored method, require extensive time, but today's marketing practices require a more direct and less time consuming method.

One solution to this time problem is the corrosivity tester shown in Figure 11. A simple, direct means for determining product corrosiveness usually within twenty-four hours, the corrosivity tester provides an index of the

100

corrosiveness of the product through application of basic electrochemical principles concerning galvanic corrosion. For many products a simple test is sufficient, but some products require additional information of product corrosion.

The corrosivity test method is based on the theory that different or dissimilar metals in an electrolytic solution (the product) create a galvanic potential difference, which, when coupled electrically (through the metal can) induces a current to flow and provides the driving force to produce corrosion. Thus, measurement of galvanic current flow under controlled conditions between tin and steel or between tin, steel and solder electrodes immersed in the product provides an index of the corrosiveness of the product with reference to the metals present in the can. Potentials of the galvanic cell electrodes determined potentiometrically with respect to a calomel reference electrode during the corrosivity test provide additional information necessary to establish the type of corrosion mechanism that exists in the product.

The corrosivity test galvanic cell consists of a one-pint (473 ml) Mason jar, the opening of which is sealed with a large rubber stopper containing the electrode assembly, a salt bridge tube for a reference electrode and gas flushing tubes (Figure 12). Modification of the test cell may be made, depending upon the test data required. Either the two-element tin-steel or the three-element, tin-steel-solder electrode assembly may be used. When electrode potential data are not required, the salt bridge tube and reference electrode are omitted.

The corrosivity tester has been used to study the effects of various product components and also the effects of inhibitors. Some of these variables studied in soft drinks include the effect of copper (Figure 13), effect of nitrates on product corrosivity (Figure 14) and the effect of Azo dyes (Amaranth)

By use of the corrosivity tester, packers have been assisted in reformulating their products to reduce the corrosive components or inhibit the product corrosivity to a level permitting satisfactory packaging in metal cans. The control of product corrosiveness by these means may be accomplished to a large degree with formulated food and nonfood products. The choice of propellents for aerosol products in some cases may influence corrosion by product interaction and also must be given consideration.

Little can be done with natural food products in the way of additives to reduce corrosion; thus control through the exercise of precautions avoids product contamination by corrosion accelerators such as sulphur or copper during the growth period, product preparation operations and product canning operations.

Container Specifications: Proper choice of materials and container design do much to limit corrosion. Container selection is not limited to controlling only the corrosive character of the product, but necessity for color or flavor preservation and other special problems may outweigh strictly corrosive considerations and result in shortened shelf life. Use of pure tin solder instead of 2 percent tin—98 percent lead solder may be required to reduce corrosion reactions. Selection of container materials,
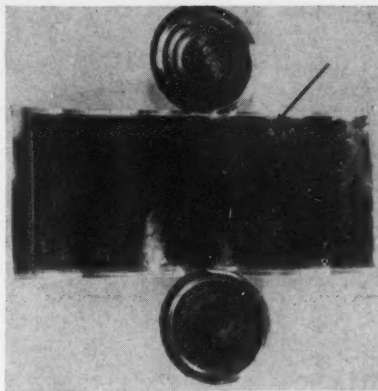
Figure 1—Perforations through body wall of enameled container caused by localized corrosion.
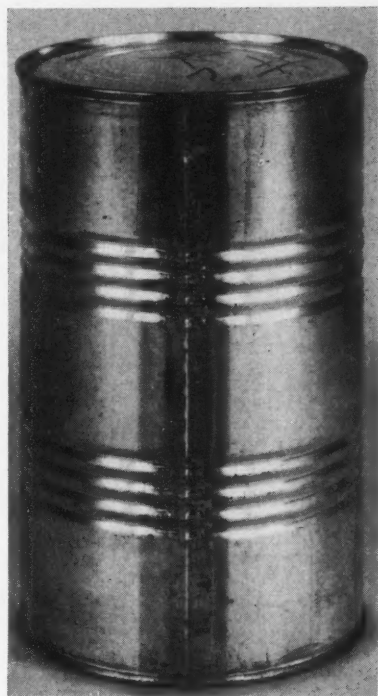
Figure 2—Springers or hydrogen swells are indicated by bulging of the can ends caused by hydrogen gas formation.
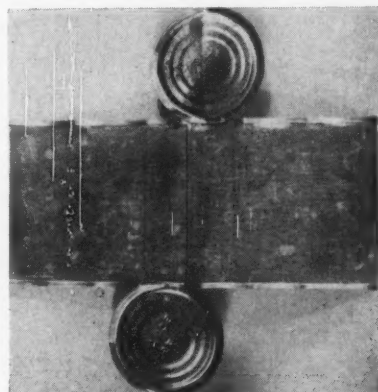
Figure 3—Internal detinning through enamel film on ends and on plain tinplate body.
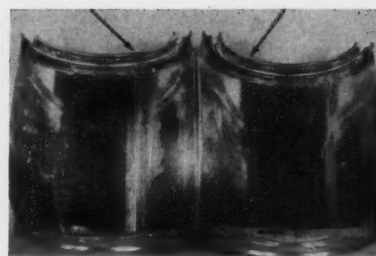
Figure 4—Ferric oxide rust spots on paint can ring indicated by arrows.
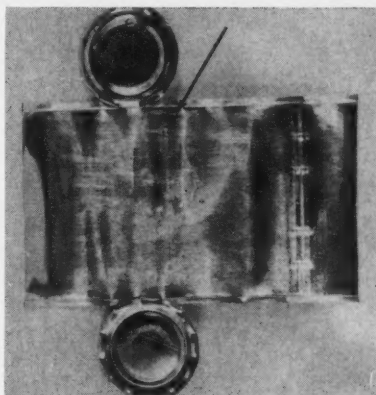
Figure 5—Mild corrosion occurred when product lifted enamel film.
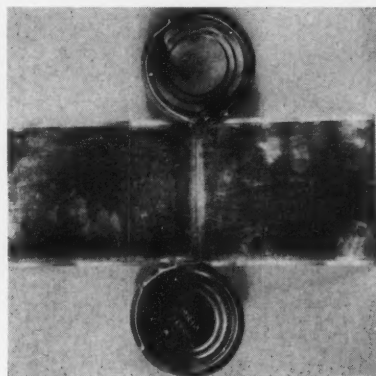
Figure 6—Staining (tin sulfide) occurred on the plain tinplate body and through the enamel film on the ends.
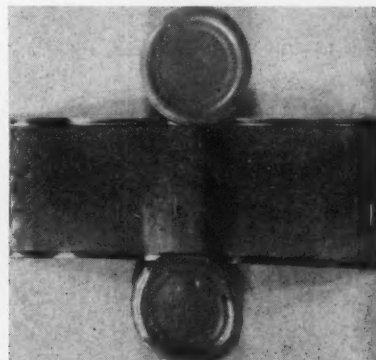
Figure 7—Tinplate body is stained through the enamel film. Top end shows discoloration (iron sulfide) on the enamel film surface.
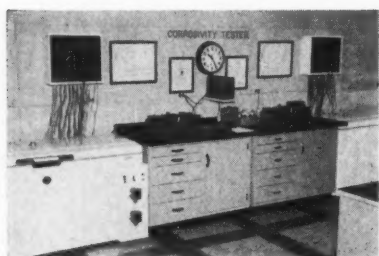
Can Corrosion—

particularly for new products about which little is known, is aided by the corrosivity tester which in 24 hours gives an indication of the position tin, steel and 2/98 solder assume in the product corrosion mechanism.

Food Products: With food products packed under essentially anaerobic conditions, an impervious organic coating is required to control perforations. Thickness of the tin coating is less a factor here than the base steel composition.

Base steel is classified by plate chemistry into three types: (1) the low metalloid type L is used for the very corrosive products, (2) the rephosphorized or MC type is used where strength is the prime requirement and the product is only mildly corrosive, (3) the MR type is used for the remainder. Tin coating thickness on the steel base plate varies from 15 to 75 millionths of an inch. A bar graph of this plate chemistry is shown in Figure 16.

Hydrogen swells are controlled in plain cans by use of greater tin coating thickness (60 millionths of an inch or better) for the strong detinning products. Where detinners are packed in organic coated cans for organoleptic considerations (odor, flavor, color, appearance), springer failure will usually give way to perforation failure as the organic coating is made more impervious.

Staining is controlled to some degree by chemical treatment of the tin plate after plating and fusing and by use of special organic coatings. Zinc oxide in these special films reacts with the sulphur from the product and prevents the sulphur from reaching the tin to form dark tin sulfide. Discoloration is controlled by the same means used for controlling staining.

Internal rusting of tinplate cans is unusual with food products. Where a problem exists, rusting can be controlled by use of greater thickness tin coated plate or by use of organic coatings.

Enamel lifting is controlled through selection of organic coatings resistant to product softening and decrease in organic coating permeability.

Non-food Products: With non-food products, container selection is in general dependent upon product corrosive-

ness, pH of the product and whether or not the product will soften or otherwise impair an organic coating. The effect of product-container reaction can have a serious result on product color or odor which can limit the selection.

Contrasted to food products, the non-food products usually are packaged with little or no oxygen removal and are not necessarily hermetically sealed. The variety of corrosive conditions is controlled by use of chemically treated steel plate, terne plate, black plate and tinplate. In addition, control of any of the various types of corrosion discussed often are effected by use of inhibitors or anti-oxidants added to the product.

Perforations can be controlled in some products by use of organic coatings as with foods, but the mechanism here is different and is a strong concentration cell established by either oxygen and/or inhibitor differential concentration. Pore free plastic bag inserts are used in cans in some cases to provide perforation control.

Hydrogen swells are not usually a problem with non-food products, but detinning can be severe. Organic coating or substitution of CTS or terne plate is the control measure.

Staining is not considered a problem with non-food products; however, discoloration or formation of any loosely adhering corrosion product including rust often is a problem. Rust or other loose deposits usually form in the headspace area; coating of the top end with an organic film usually will control the action.

Packaging Methods—Storage: Corrosion control through control of packaging methods and storage conditions must include control of product preparation, product canning, canned product processing, canned product handling and canned product storage.

Product Preparation

Corrosion accelerators such as copper and sulphur compounds must be removed from natural products during preparation by washing, and precautions must be exercised to avoid pick-up of corrosion contributory compounds from the equipment or treatment materials. Raw materials control is necessary with formulated products because process variations in chemical manufacture may be reflected in corrosion properties of the finished product. It may, in some cases, be necessary to provide special treatments during product preparation to insure removal of oxygen which has a strong effect on corrosion. The effect of oxygen on the corrosiveness of soft drinks as determined by the corrosivity tester is shown in Figure 17.

Product Canning and Canned Product Processing

Exclusion of oxygen to reduce corrosion is perhaps the biggest problem in canning food products with pick-up of copper from product handling equipment as second largest problem. Research has established many of the factors necessary to provide a satisfactory package. Temperature of product and syrup at fill, product-Headspace relationship, vacuum or gas packing of product and undercover gassing are some of these factors. Heat processing usually is under strict control, and it is necessary only to exercise precautions that effective cooling of the can is accomplished after cooking.

With non-food products, oxygen removal normally is not practiced except

Figure 8—Rust spots formed at pores in tin coating.

Figure 10—Plain tinplate can is badly stained. No rust present.

Figure 11—Corrosivity tester used to determine product corrosiveness.
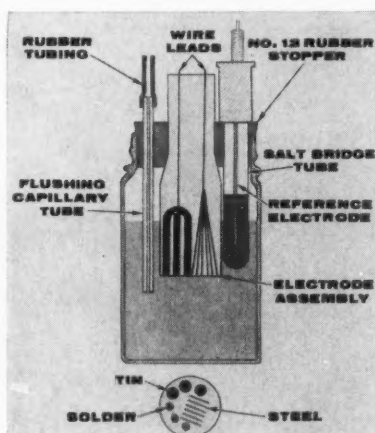
Figure 12—Cross section of corrosivity test cell.

Figure 13—Effect of copper on corrosiveness of soft drinks.
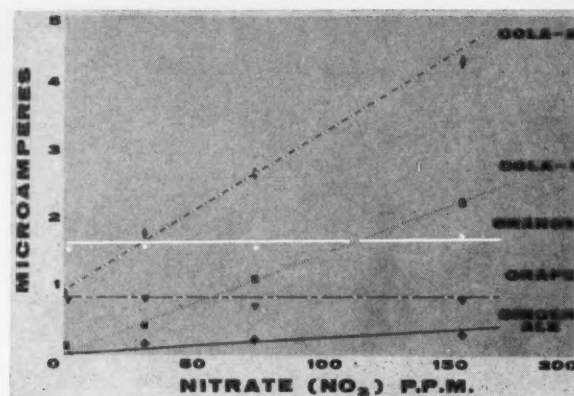
Figure 14—Effect of nitrates on product corrosivity.

Can Corrosion—

(Continued From Page 102)

for vacuum crimping or purging of aerosols, but its effect may be controlled in some cases by oxygen-scavenger additions to the product. Here again, copper pick-up from equipment can be a serious factor.

The embossing of container ends for product identification may be controlled to a degree by use of nylon die pads, but care must be exercised not to fracture the organic coating when packing corrosive products. Misaligned, cocked or sharp dies and heavy impressions will lead to organic coating fracture and perforation failure as illustrated in Figure 18.

Canned Product Handling and Canned Product Storage

Handling of the canned product, especially corrosive products in organic coated cans, must be controlled to avoid sharp dents which can result in coating fracture. These areas where organic coating damage occurs will result in preferred corrosion sites with failure by perforation as shown in Figure 19.

Storage conditions should be regulated to control temperature at as constant a low value as possible. Electrochemical and chemical reactions are less active at lower temperatures. Changing temperatures during storage result in thermal agitation of the product which in turn increases corrosion through removal of polarization effects at anode and cathode areas. Headspace corrosion in products prone to this type corrosion

will increase with changing temperature conditions because this will usually produce more condensation in headspace than constant temperature conditions.

External Corrosion Control Measures

The most common problem, rusting, has increased because use of differentially coated electrolytic tinplate has re-

Figure 16—Chemistry of base steels used in containers.

placed regular hot dipped tinplate. This change has meant a reduction in external tin coating thickness from approximately 60 millionths to 15 millionths of an inch. The internal tin coating thickness was kept at 60 millionths. Porosity increases and atmospheric corrosion resistance decreases as tin coating thickness is reduced; however, the thickest tin coatings do not eliminate porosity entirely, but only reduce it. The control measures discussed will prevent corrosion for a period under most severe conditions but will not eliminate corrosion entirely for an unlimited time.

Protective Coatings

Protective organic coatings on light weight tin coated plate provide better protection than that afforded by the thickest tin coating. Over-all post organic coating provides greater protection than over-all pre-coating. Paper labels may or may not provide protection. Tests have demonstrated that label papers not completely freed from chemical residue may accelerate corrosion. One paper tested inhibited corrosion. Control also is possible with exterior protective packaging, a system that is relatively expensive.

Chemical Treatments

Chemical treatment of the filled cans after processing with weak solutions of sodium chromate, sodium nitrite, one of the polyphosphates, sodium benzoate or mixtures of these chemicals with cooling canal water have been used with varying success depending upon local water

Figure 15—Effect of Azo (amaranth) dye on corrosiveness of strawberry drink.
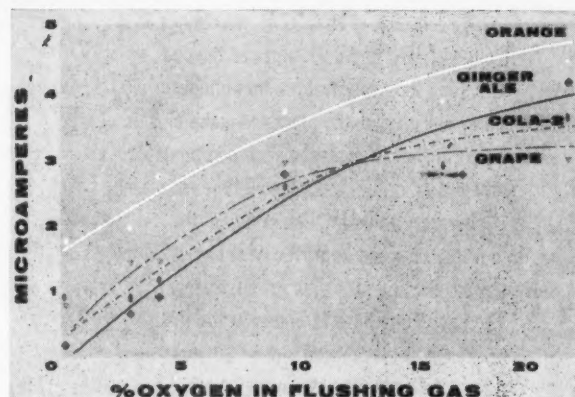
Figure 17—Effect of oxygen on soft drink corrosiveness.

Figure 18—Coating fracture with perforation failure may result from sharp dies and heavy impressions used in embossing container ends.

Can Corrosion—

(Continued From Page 104)

conditions. The exact mechanism of control (i.e., absorbed films vs oxide formation) has yet to be resolved. However a minute residue apparently will stay on the can, and upon being wetted by condensation the chemicals are available again to assist in inhibiting corrosion. For severe conditions, heavier concentration dip solutions have proved effective.

Control of rusting by use of oils has been practiced with varying success. Two methods have been used: use of a volatile oil in retorts and use of a light oil application by spray, dip or wipe after processing, cooling and drying. If the oil will wet and fill the pores in the tin plate, rusting probably will not take place although the tin areas may not have a film on them.

Cannery Technique

Cannery technique also can be considered a control method although this is almost in the class of good housekeeping. Avoiding contamination of cooling and retort waters with product, spillage of product which remains on the can, removal of tin or organic coating in double seaming, retorting, or handling and use of rusty equipment all constitute areas for control.

Storage Conditions

Control of storage conditions is perhaps the most important. If storage conditions are allowed to become severe, cans treated by any of the control systems mentioned eventually will rust.

Figure 19—Sharp dents from handling may cause coating fracture with resultant perforation.

Control of relative humidity is of prime importance to prevent condensation or sweating; moisture will condense on can whenever their temperature falls below the dewpoint for the surrounding atmosphere.

Summary

Can corrosion which affects product odor, flavor or appearance and/or container appearance must be considered with springer or perforation container failure in determining acceptable container performance. Container specification for a product often is a compromise based on the types of corrosion encountered and is competitively limited by economic considerations. Corrosion is caused by many factors, such as product contamination, unfavorable product formulation, unfavorable processing or packing conditions, unfavorable handling or storage conditions and variable natural corrosiveness of products. Control of corrosive action of the product can be obtained through matching product with can material characteristics in the most economical manner. Also product corrosiveness may be modified by product formulation changes, addition of inhibitors or oxygen scavengers to the product, control of the method of product preparation and/or method of packing and by control of canned product handling and storage.

DISCUSSIONS

Question:
Wouldn't it be better to form the cans at the cannery?

Answer:
Cans are made at the cannery or right next door in some cases, and this practice eliminates can damage which might occur in shipping. Economically, this is possible only where the volume of can usage justifies the can manu-

facturing facilities' expense. Technologically, a fairly large integrated can manufacturing plant is able to produce the more economical containers.

Question:
What happens to flux used in soldering?

Answer:
Very careful metered control of the amount of flux applied limits the residue. Fluxes used for soldering cans are designed to leave an essentially noncorrosive residue after soldering.

Question:
Are beer cans deep drawn?

Answer:
Yes, but this is a complicated, costly multiple draw operation.

Question:
Do you test for continuous organic film?

Answer:
Yes, organic film continuity tests are made.

Question:
Will the enamel crack more from dents in the can when it is hot or when cold?

Answer:
Sharp dents will result in loss of enamel adhesion but rarely cracks. Enamels prone to cracking in forming operations usually are more susceptible when cold.

Question:
Are coffee cans tinplated?

Answer:
Yes, these cans are usually made from plate containing 15 millionths of an inch tin coating.

Question:
When is lithographing done?

Answer:
Lithographing is done in the flat on large sheets of tinplate. These sheets are coated in two and three color presses similar to those used for paper. Twenty to thirty-five can bodies are obtained from one sheet.

Question:
What is the thickness of tin on No. 1 per basis box?

Answer:
The thickness of tin is 60 millionths of an inch.

Question:
Can you deep draw tinplate?

Answer:
Deep draws are possible in multiple draw operations. However, because of economical considerations, only one operation limited draws are made.

Question:
Does it hurt to leave fruit juice in can in the refrigerator?

Answer:
There is no hazard to health to leave the fruit juice in the can. However, appearance of the container and taste of the product may change depending on the time the opened can is stored.

Some Properties and Uses of

Chlorinated Polyether*

Abstract

Discusses physical properties, chemical resistance and field application data of a new chlorinated polyether. Comparative dimensional stability under relatively high operating temperature conditions with other plastics is given. Discusses use of the material in valves, bearings, precision gears, and corrosion resistant coatings.

POLYBISCHLOROMETHYL OXETANE,* a new commercially available thermoplastic, can be introduced to those hearing about it for the first time as a chlorinated polyether. The material has been chemically reformed from pentaerythritol into the ether molecule shown in Figure 1. It contains approximately 46 percent chlorine by weight. The position of each chlorine atom in a chloromethyl group attached directly to the central carbon atom makes for excellent chemical stability. The polymerized form exhibits the same unusual chemical inertness. It has high molecular weight, is linear in nature and crystalline in character.

Some of its physical properties are compared with those of other more generally known plastics in Table 1. In addition to adequate tensile strength, hardness, flexural strength, resistance to deformation and resilience, it has unusually low water absorption, low permeability, high temperature resistance

★ Revision of a paper titled "Some Field Experiences on Penton and Penton Lined Equipment" by C. S. Miller and J. B. Martin, Hercules Powder Co., Wilmington, Delaware, presented at the 15th Annual Conference, National Association of Corrosion Engineers, March 16-20, 1959, Chicago, Ill.

* Penton, Hercules Powder Co. registered trademark

and good abrasion resistance. It can be easily molded, heat formed, welded and machined. It is inert to almost all acids, alkalies and solvents and can be used with more reagents and solvents than any single metal alloy or glass. Its dimensional stability is as good as or better than that of other commercially available thermoplastics.

Figure 2 shows physical changes in dimension due to cycled extremes of temperature and humidity. The diameter of the 2-inch test discs changes less than a mil when subjected to 24-hour periods of hot humid air followed by 24 hours of cold. Similar parts boiled for a month show dimensional changes of about the same amount. Resistance to cold flow ranks favorably among the plastics and its heat distortion temperatures are well above the normal thermoplastic range. In Figure 3, we see comparative resistance to abrasion caused by a metal wheel rubbing against a wheel of various plastics. Laboratory measurements on notch sensitivity to impact show the material is in the same range as unplasticized vinyls and vinylidines.

Polybischloromethyl oxetane can be handled in any of the conventional methods of forming and fabrication except solvent welding. No practical solvent or plasticizer has been found to date. It can be molded with accuracy, detail and finish, eliminating all or most of the machining operations normally associated with equivalent metal

parts and can be compounded with fibres such as glass or ceramic or with fillers such as graphite.

The material shows remarkable adhesion to hot metals. It can be applied by whirl sintering techniques to metal parts forming tough corrosion resistant coatings 10 to 40 mils thick. Commercial coatings of any desired thickness can be applied by transfer molding or flame spray techniques. An unusual property is resistance to loss of bond by corrosives. It has been found that when corrosive products are in contact with a damaged coating the metal beneath is attacked, but there is no loss of bond in the areas surrounding the damage. Its melting temperature of 360 F. is lower than that of the nylons, but there is usable tensile strength up to 300 F.

In Figure 4, the plot of operating pressure for a solid valve shows a very flat slope, almost to the melting point. Because of the chemical inertness of Penton to elevated temperature hydrolysis articles for hot service conditions can be designed with practical wall thicknesses and long term reliability. Even at temperatures above 250 F. shapes have performed satisfactorily for years. Wall thickness for Penton valve bodies will be about the same as those used on equivalent alloy cast bodies which are normally designed for minimum porosity rejects.

Long term testing for high temperature creep shows in Figure 5 an outstanding dimensional stability at the lower design stress levels commonly used in chemical processing equipment.

$$\left(-CH_2-\underset{\underset{CH_2Cl}{\overset{\displaystyle CH_2Cl}{|}}}{\overset{|}{C}}-CH_2O- \right)_n$$
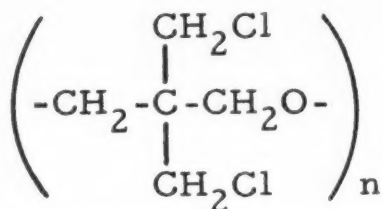
Figure 1—Chemical structure of chlorinated polyether.
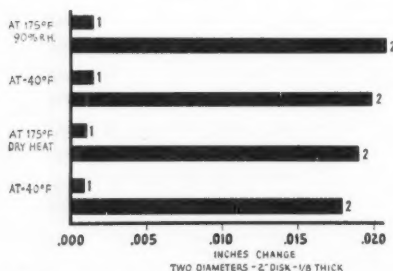
Figure 2—Dimensional stability of chlorinated polyether. Each exposure was for 24 hours. Number 1 bars represent polybischloromethyl oxetane; Number 2 bars, polychlorotrifluoroethylene.

TABLE 1—Plastics Properties Chart

Physical Properties	Units	Polybischloromethyl Oxetane	Unplasticized Vinyl Chloride	Fluoro Chloro Hydrocarbon	Nylon
Tensile Strength					
73 F Dry	psi	6,000	8000–9000	4500–6000	10,900
21 F Wet Yield	psi	3,000	—	750	3,500
Elongation					
73 F Dry	%	35	20–30	25–35	90
212 F Dry	%	200–250	Too soft to test	> 300	> 300
Tensile Modulus					
73 F Dry	psi x 10⁻³	160	400	190–225	430
212 F Wet	psi x 10⁻³	30	Too soft to test	5	18
Flexual Strength 73 F	psi x 10⁻³	11	12–15	8	14
Stiffness 73 F	psi x 10⁻³	200	450	180	250
Water Absorption	%	0.01	0.1	0.00	1.5
Heat Distortion Temperature					
264 psi	F	185–200	145–185	Not reported	150
66 psi	F	300	165		360
Izod Impact (Notched) 73 F ft. lb./in. notch		0.5	0.5–0.8	3–5	1.0
Izod Impact (Unnotched) 73 F ft. lb./in. notch		> 33	—	—	> 40
Rockwell Hardness 73 F	—	R100	R120	R110	R118
Deformation Under Load. 122 F, 2000 psi	%	1.4	0.6–0.9	—	1.4
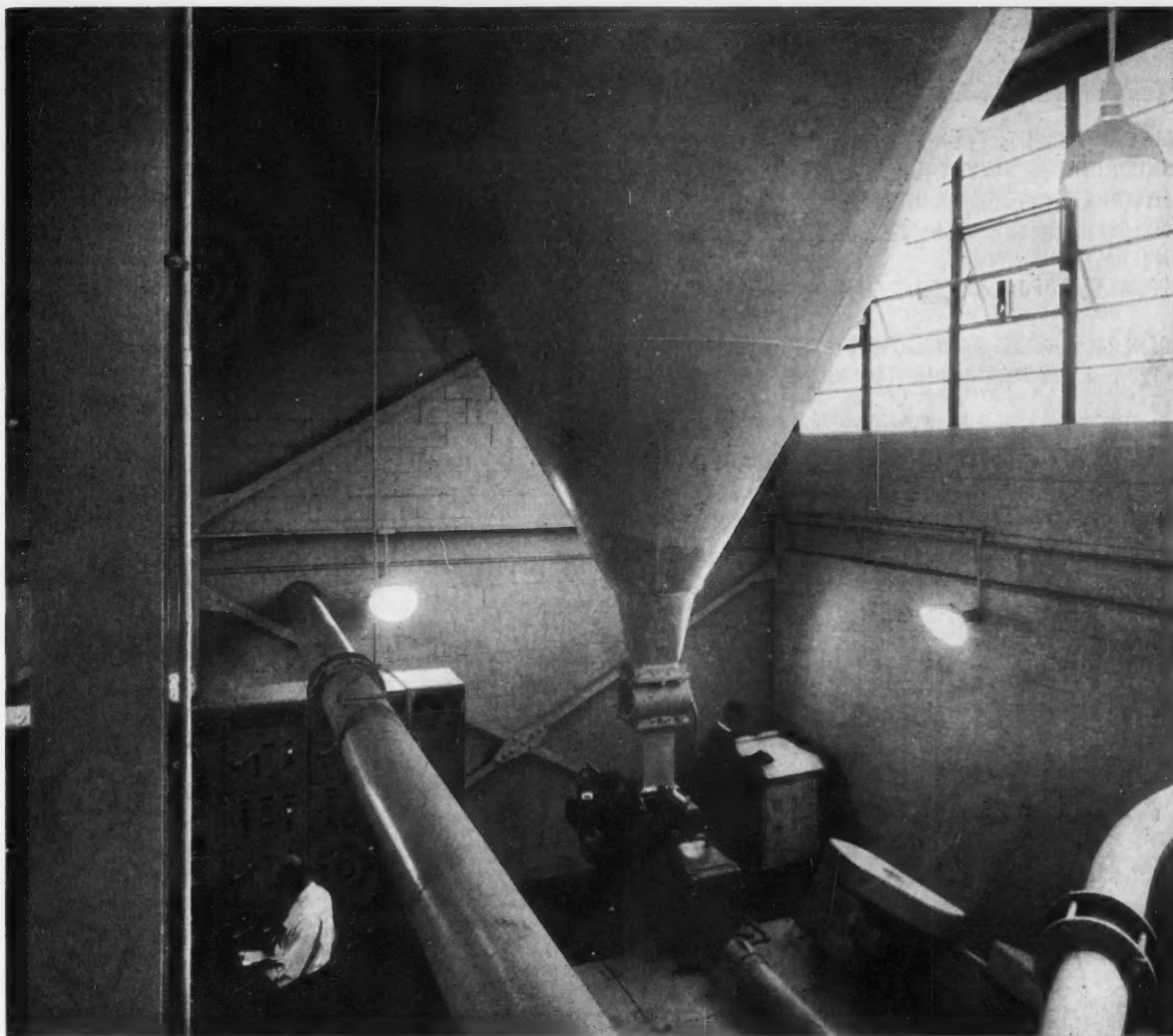
WHEN THE BEST IS REQUIRED
PARLON IS FIRST CHOICE

Here's a photograph worth a million words. It shows the Chemical Feed Room at the Middlesex County Sewerage plant at Sayreville, N.J. Throughout this plant a protective coating must meet the challenge of chemical fumes. That's why Socony Paint Products Company's Sovaklor Chemical Resistant Coatings based on Parlon® chlorinated rubber were selected for walls, beams, hoppers, pipes and other equipment. Perhaps Parlon's long life, resistance to corrosion, and ability to cover almost any type of surface material can solve your maintenance problems. Your supplier of quality paint can tell you more about Parlon, or write direct to Hercules.

Cellulose Products Department

HERCULES POWDER COMPANY
INCORPORATED

900 Market Street, Wilmington 99, Delaware

CH 59-5

ABRASION OF PLASTICS
(AFTER 7 HRS OF TEST) VOL. LOSS (CC × 10³)

LINEAR POLYETHYLENE (ZIEGLER PROCESS)	2
CHLORINATED POLYETHER	9
NYLON A (SWISS CAPROLACTAM)	13
NYLON B (CAPROLACTAM)	15
NYLON C (NYLON 6-6)	25
EPOXY B (EPOXY MOLDING COMPOUND 68% CLAY 3% NYLON FLOCK FILLER)	45
GENERAL PURPOSE PHENOLIC WOOD FLOUR FILLED	57
EPOXY A (EPOXY MOLDING COMPOUND 60% CLAY 10% NYLON FLOCK FILLER)	81
DIALLYL PHTHALATE, ORLON FILLED	149
FLUOROCARBON (POLYTRIFLUOROMONOCHLOROETHYLENE)	159
STYRENE ACRYLONITRILE - RUBBER COPOLYMER	306
HIGH HEAT, HIGH IMPACT RUBBER MODIFIED POLYSTYRENE	642 {TESTED ONLY 6 HRS}

Figure 3—Comparative abrasion resistance of plastics. From M. A. Marcucci, *SPE Journal*, 14, No. 2, 32 (1958).

PRESSURE TEMPERATURE RATINGS
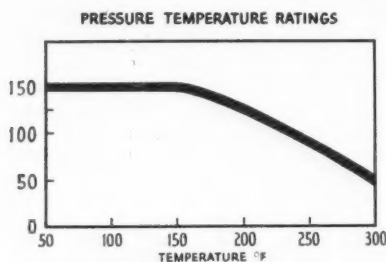
Figure 4—Pressure temperature ratings of valves made of chlorinated polyether. Scale on left gives psi pressure.

Figure 5—Chlorinated polyether creep data for various loads at 280 F.
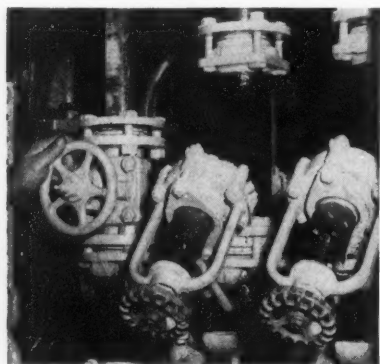
Figure 6—Injected molded cast iron flanged body diaphragm, lined with chlorinated polyether.
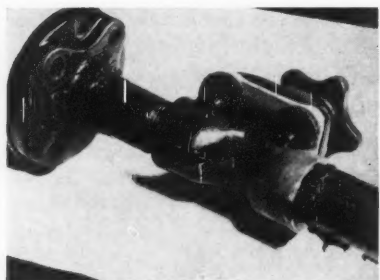
Figure 7—Injection molded screwed body diaphragm valve made of chlorinated polyether.
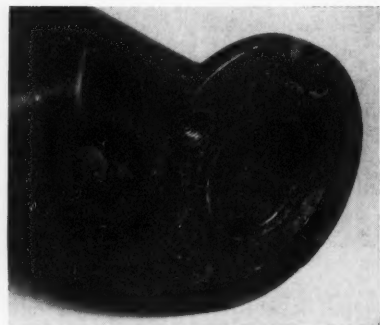
Figure 8—Whirl sintered coating on a fabricated steel flanged tee.

Figure 9—Flamed spray coating of chlorinated polyether over a solid nickel scraper blade in a rotary vacuum dryer.

Chlorinated Polyether
(Continued From Page 108)

In Figure 6, an injection molded Penton lined cast iron flanged body diaphragm valve has been mounted above a glassed steel vessel used for a hydrocarbon chlorination. At service temperatures from 35 to 85 C exposure is to C Cl₄, HCl and wet Cl₂. This valve has been in service more than three years. Adjacent piping and valves are of porcelain, furan resins, glass and glassed steel.

Another type of molded lined valve was installed in a storage tank area for use in 32 per cent HCl containing small amounts of nascent chlorine at ambient temperature. When it failed after 33 months because a gasket leak at one flange resulted in destruction of the outside metal, the Penton lining had been unaffected.

The injection molded solid screwed body diaphragm valve shown in Figure 7 was installed in an HCl feed line with polyvinylchloride pipe. When process malfunction caused hot tower product to flow back through this line and valve, the valve was undamaged but the PVC piping failed. The valve was reinstalled and remains in service after 30 months.

Figure 8 shows a whirl sintered coating, inside and outside on a fabricated steel flanged tee installed in a mixture of weak acetic acid and ethyl acetate at 30 C. The interior coating was in good shape after two years. The tee was removed after mechanical damage to the outside coating exposed the metal to atmospheric corrosion attack.

Figure 9 shows a .027-inch flame sprayed coating over a solid nickel scraper blade in a rotary vacuum dryer. The conditions within the drying cycle require corrosion resistance and the fine ground material being dried is 0.6 as hard as glass. The coating was in good shape at the end of four months and was worn away in the areas shown at the end of five months' service. It is interesting to note that the nickel blades suffer attrition at the rate of .042-inch in the same period.

DISCUSSIONS

Comments by Alfred D. Bundy, Industrial Rayon Corp., Cleveland, Ohio:

We have observed a thin, skin-type delamination on molded test bars of polybischloromethyl oxetane after exposure in several rayon processing solutions. Has this effect been observed on other articles molded of this material?

Reply by C. S. Miller and J. B. Martin:

Proper molding conditions for this oxetane material differ somewhat from the molding conditions in normal use for other thermoplastics. It changes from the melt to the crystalline form for consistently good moldings when the die temperature is held at about 200 F.

We have seen evidence of a skin type delamination when oxetane articles have been molded into a cold die. We have never seen evidence of delamination from moldings made using the recommended mold conditions and temperatures.

•

CORROSION ABSTRACTS

INDEX TO CORROSION ABSTRACTS

Vol. 15   November, 1959   No. 11

1. GENERAL

1.2 Importance

1.2.5, 3.8.4

Hydrogen Production in the Calcium and Magnesium-Nitric Acid Reactions. M. N. Myers. General Electric Co. Hanford Atomic Products Operation. U. S. Atomic Energy Commission Pubn., HW-38753 (Del.) August 19, 1955 (Declassified with Deletions Jan. 30, 1958), 5 pp. Available from Office of Technical Services, Washington, D. C.

For greater understanding of possible explosion hazards, data are needed of the volume of hydrogen evolved in the cadmium and magnesium reactions with nitric acid. Nearly five liters of hydrogen per mole of calcium are produced when $16M$ nitric acid reacts with calcium metal. The hydrogen evolved slowly increases with decreasing nitric acid to below $4M$ nitric acid, when a rapid increase occurs. The magnesium-nitric acid reaction produces only one liter of hydrogen per mole of magnesium with $2M$ nitric acid and the volume of hydrogen decreases with increasing nitric acid concentration.—NSA.
16907

1.2.5, 6.3.20, 3.4.6

Reactions of Metals with Oxygen and Steam. Quarterly Rept. No. 5 (Rept. No. 15) for July-Sept. 1958. Fred E. Littman and Franklin M. Church. Stanford Res. Inst. for Oak Ridge Nat'l. Lab. U. S. Atomic Energy Commission Pubn., AECU-3882, October 22, 1958, 6

pp. Available from Office of Technical Services, Washington 25, D. C.

The autoignition limits of Zircaloy-2 and -203 were investigated using foil and rods, under static and dynamic conditions. The results were marked by an unusual variability, Zircaloy-2 rods ignited at pressures as low as 650 psi of oxygen, but sometimes failed to ignite at 1500 psi. Zircaloy foil ignited at pressures above 750 psi of oxygen under static conditions. Under dynamic conditions, autoignition occurred at pressures as low as 50 psi, but at other times did not occur up to 500 psi. The reasons for this erratic behavior are not known for certain, but indications are that it is caused by minute variations in the composition of the material, which alter some physical characteristic of the metal (such as brittleness). Because of this lack of reproducibility, variation of the autoignition limits with oxygen concentration have not been reliably established. The importance of changes in

---

Abstracts in This Section are selected from among those supplied to subscribers to the NACE Abstract Punch Card Service. Persons who are interested in reviewing all available abstracts should write to NACE for information on this service.

---

surface-to-volume ratios is also obscured by this lack of reproducibility. At this time attempts are being made to overcome this by using very large changes in the ratios. (auth).—NSA. 17460

1.6 Books

1.6, 2.3.9

Radioisotopes in Scientific Research. R. C. Extermann, Editor. Proceedings of the International Conference Held in Paris in September 1957 under the Auspices of the United Nations Educational Scientific and Cultural Organization. Vo. I: Research with Radioisotopes in Physics and Industry. Book, 761 pp., 1958. London: Pergamon Press, Ltd.; New York: Pergamon Press, Inc.

Contents include: G. V. Kidson and R. Ross: Self-Diffusion in Polycrystalline Platinum; I. N. Frantsevich, D. F. Kalinovich, I. I. Kovensky and B. B. Penkovsky: An Investigation of Electric Transport in Solid Solutions of Metals Using Radioactive Isotopes; V. T. Borisov, V. M. Golikov, B. Y. Ljubov and G. V. Shtsherbedinsky: Study of Grain-Boundary Diffusion in Metals; S. Z. Bokstein, S. T. Kishkin and L. M. Moroz: Effect of Metal Composition and Structure on Grain-Boundary Diffusion; P. L. Gruzin, Y. F. Babikova, Y. A. Polikarpov and G. B. Fedorov: Investigation into Carbon Atoms Mobility and Atomic Interaction in Alloys by the Use of Tracer Technique; K. M. Mahmoud and R. Kamel: Tracer Diffusion of Cadmium[115] in Pure Cadmium; A. A. Zhukovitsky, M. E. Janitskaya and A. D. Sotskov: Application of Radi-oactive Isotopes in Solving Diffusion Problems in Metal Theory; Dora M. Brasher, C. P. De, A. H. Kingsbury and A. D. Mercer: The Use of Radioactive Tracers in the Study of Passive Films on Metals; J. Golden and G. W. Rowe: A. Radioisotope Study of the Effect of Surface Conditions During Wear of Tungsten Carbide; V. S. Vavilov, L. S. Smirnov, A. V. Spitzin, V. M. Patskevitch and M. V. Chukichev: The Structural Defects in Germanium Mono-Crystals Irradiated by Beta-Particles and Fast Neutrons and the Influence of these Defects on Electron-Hole Recombination; V. S. Vavilov, L. S. Smirnov and V. M. Patskevitch: Energy of Ionization by Beta-Particles in Crystals of Germanium and Silicon; T. Pyle and R. Shuttleworth: The Interaction of Silver Impurity-Atoms with a Copper Solvent; L. A. Schwarzman: Thermodynamic Studies of Metallurgical Reactions.—MA. 17251

1.6, 3.5.4

The Effects of Radiation on Materials. J. J. Harwood, H. H. Hausner, J. G. Morse and W. G. Rauch, Editors: Proceedings of a Colloquim Held in March 1957 in Baltimore, Sponsored by the U. S. Office of Naval Research and the John Hopkins Univ. Book, 355 pp., 1958. Reinhold Publishing Corp., New York and Chapman and Hall., Ltd., London.

Contents: G. J. Dienes, Defects in Solids and Current Concepts of Radiation Effects; J. C. Wilson, Experimental Approaches to Radiation Effects; D. S. Billington, Radiation Effects in Metals and Alloys; M. T. Simnad, Influence of Radiation upon Corrosion and Surface Reactions of Metals and Alloys; R. Smoluchowski, Radiation Effects in Dielectric Solids; H. Y. Fan and K. Lark-Horovitz, Irradiation Effects in Semi-Conductors; C. E. Weber, Effects of Radiation on the Core Components of Nuclear Reactors; G. R. Hennig, Effects of Radiation on Shielding, Moderators and Auxiliary Components of Nuclear Reactors; M. Burton, Experimental Techniques and Current Concepts: Organic Substances: A. Charlesby, Effect of Radiation on Behavior and Properties of Polymers; A. J. Restaino, Radiation-Induced Graft Co-polymerization; Helen C. Friedemann, Bibliography: Effect of Irradiation on Solids.—MA. 17395

2. TESTING

2.3 Laboratory Methods and Tests

2.3.2

Corrosion Testing with Aerosols. Description of a New Corrosion-Testing Cabinet. (In German.) W. Hess. Metalloberfläche, 11, No. 3, 101-104 (1957.

The design, construction, and operation of the cabinet is described. Its principal feature is that the salt spray or other corrosive medium is produced as an aerosol in the optimum particle-size range—5-25μ—for corrosion testing; it has the usual humidity, temperature, and time-cycle controls. Some test results are discussed.—MA. 17002

2.3.7, 5.3.4

Spiral Bending Test for Electrodeposited Coatings. J. Edwards. Trans. Inst. Metal Finishing, 35, 101-106 (1958). Bull. Inst. Metal Finishing, 8, No. 2, 101-106 (1958) Summer.

Describes simple method of measuring ductility of rather brittle electrodeposited coatings. Plated strip is bent around former in shape of an equiangular (logarithmic) spiral and radius of curvature at which coating cracks is read off directly from graduations on former. Percentage elongation at this point is simply calculated from radius of curvature and thickness of plated strip. Details are given of construction of former, preparation of specimens and method of carrying out test. Both mild steel and brass were used satisfactorily as basis in testing bright nickel deposits; an undercoat of copper on steel appeared not to affect substantially ductility values observed. Experience with test to date is summarized.—INCO.   16479

2.3.8, 8.4.3
Full Process Control Wins Pilot-Scale Role. C. S. Cronan. Chem. Eng., **65**, No. 14, 78-79 (1958) July 14.

Duplicating processes such as hydrofining, hydrogenation, and catalytic reforming, California Research Corp.'s pilot system is first of its kind to use monitored operation. Much of equipment was designed at CalResearch. Liquid feed enters system through diaphragm pump constructed of Type 316. Reactor, of Type 321 and 347, is divided into preheater, catalyst bed, and afterheater. High-pressure separator is a Type 347 pot. Flow sheet.—INCO
     17200

2.3.9
Electron Diffraction and Optic Data on the Thickness of Oxide Films on Metals. (In Russian.) V. V. Andreeva and N. A. Shishakov. Inst. of Physical Chemistry, Moscow. J. Phys. Chem. (Zhur. Fiz. Khim.), **32**, 1671-1672 (1958).

Measurements were made of the oxide film thickness of aluminum gold, iron, platinum and titanium in vacuum (10^{-7} mm mercury column) at atmospheric pressure with the relative humidity 40 to 45 per cent and at room temperature. NSA.   17178

2.3.9
Use of Structural Electron-Diffraction Analysis in Metallography. (In Russian.) M. I. Tsypin. Metalloved. i Obrabotka Mettalov, No. 5, 62-64 (1957).

A brief review of underlying principles, the construction of the EM-4 electron-diffraction camera and examples of the use of the method (particularly the study of oxide films on aluminum and on aluminum-magnesium and aluminum-magnesium-berryllium alloys).—MA   17067

2.3.9, 3.7.4, 3.5.9, 6.2.5
Structural Changes in Austenitic Steels During Creep Testing. W. Koch, A. Schrader, A. Krisch and H. Rohde. Stahl und Eisen, **78**, 1251-1262 (1958) Sept. 4. (In German.)

Report of metallographic examination of creep-test specimens in titanium- and niobium-stabilized nickel-chromium and nickel-chromium-molybdenum austenitic steels after testing for 50,000 hours at temperatures up to 700 C. Study was made of carbide reactions and formation of intermetallic compounds during creep-testing, using extraction techniques, micro-analysis, X-ray determinations and electron microscopy. Role of sigma phase in embrittling phenomena, discussion on interrelationships between metallographic changes, stress and appearance of fracture, and full details of techniques and results are included.—INCO. 17435

2.3.9, 3.8.4
Comparison of Total Emittance with Values Computed from Spectral Measurements. J. T. Bevans, J. T. Gier and R. V. Dunkle. Paper before Am. Soc. Mech. Engrs., Annual Mtg., New York, Dec. 1-6, 1957. Trans. ASME, **80**, No. 7, 1405-1414; disc. 1414-1416 (1958) Oct.

Spectral and total emittances were measured for materials exposed to various oxidation conditions. The 25 samples studied in this program consisted of typical aircraft construction materials with special surface coatings and/or thermal treatments. Untreated samples were included for comparison. Total emittances were measured at 200, 400, 600 and 800 F, while spectral reflectances were measured at 100 F. Total emittance values computed from spectral data compare favorably with measured total values. Experimental techniques utilized for both types of determinations are described and effect of temperature, sample preparation and experimental errors are discussed relative to differences obtained in results. Specimens include titanium alloys with and without aluminized-silicon paint, Type 321, bare, silver-plated and painted with black heat-resistant air-dry enamel. In discussion, G. A. Etemad (North Am. Aviation) presents data for additional samples including: Inconel X, aluminized-silicon paint on Inconel X, Type 17-4 PH, Type 17-7 PH, white paint on Type 17-7 PH, black oxide coating on Type 321; and various combinations of rhodium, chromium palladium, silver and gold plating on nickle-plated Type 321. Tables, graphs.—INCO.   17291

2.3.9
Notes on Problems Involved in Classification of Defects in Ultrasonic Examination. (In French.) H. J. Seemann & W. Bentz. Rev. Met., **54**, No. 7, 529-536 (1957) July.

Classification of defects in ultrasonic inspection; problems in practical application of echo impulse method, with examples of tests carried out on heavy steel forgings and boiler plates; most important factors to consider in ultrasonic testing are composition of alloy, manufacturing process and ultimate use of part.—BL   17062

2.3.9, 2.4.3
Improvements in, and New Applications of, the Technique of Non-Destructive Metallographic Examination. (In French.) P. A. Jacquet. Paper before Journées d'Automne, October, 1957. Rev. Mét., **55**, 531-553; disc., 553-554 (1958) June.

Detailed review of new techniques and applications of localized electrolytic pol-

ishing and replica methods for metallographic examination. Recommended electrolytic-polishing solutions and voltages are given for various metals, including nickel and nickel alloys, cobalt and cobalt alloys, cupro-nickels and stainless steels. Specific description of applications of pad technique to anodic oxidation of aluminum and anodic attack of 18/8 steels is given. Improvements in replica technique include reduction of time for taking print, simplification of film removal and film mounting for examination. New applications in laboratory (examination of foil, wire, cracks and inclusions, under polarizing microscope, electronic micrography) and works (structure of 18/8 tubes, welds in pipes, cracks in crankshaft, fracture in stainless-steel part) are discussed.—INCO.   17383

2.3.9, 3.5.4, 8.4.5
Radiochemical Instrumentation on the Post Irradiation Corrosion Loop. D. G. Miller and W. C. Judd. Knolls Atomic Power Lab. U. S. Atomic Energy Commission Pubn., KAPL-M-DGM-1, July 1, 1958, 14 pp. Available from Office of Technical Services, Washington, D. C.

A brief summary is presented of the information gained through the radiochemical instrumental techniques employed during the first run of the post-irradiation corrosion loop.—NSA. 17498

2.3.9, 6.3.15
Memorandum on the Use of X-Ray Diffraction for the Study of Titanium and Titanium Alloys. J. R. Doig, Jr. Battelle Memorial Inst. for the Assistant Secretary of Defense for Research and Engineering. March, 1958, 19 pp.

Available from Office of Technical Services, Washington 25, D. C. (Order PB 131940).

This memorandum is a condensed, selective collection of information on the applicability of X-ray diffraction to metallurgical research on titanium alloys. The first part contains suggestions on procedures for achieving optimum quality X-ray diffraction patterns, and the second part provides information collected from literature on standard or typical X-ray diffraction patterns. Recommendations are outlined for minimizing X-ray fluorescence encountered in X-ray diffraction work on titanium. The X-ray standard patterns and the structure data needed to carry out diffraction work on titanium are widely scattered in the literature. Therefore, the second half of the report was organized to serve as a guide for finding such information. Standard patterns are presented for the common titanium-rich phases. Tables, curves, and references are given on the lattice constants for alpha and beta solid solutions. For titanium compounds, references are given to X-ray data for the binary systems most frequently encountered.—OTS.   17271

2.4 Instrumentation

2.4.2
An Apparatus for Heating Small Samples to Elevated Temperatures at High Pressures. J. Fennell, N. H. Hancock and R. S. Barnes. Metal Treatment and Drop Forging, **25**, No. 155, 332-334 (1958) August.

Describes apparatus for incorporating pressure-vessel capable of withstanding internal gas pressure of 6,000 lb/sq in. at temperature of 950 C. Gas from cylinders is compressed by pump to pressure required and high temperature obtained by lowering furnace over end of pressure-vessel which contains sample. Pressure vessel was made from Nimonic 95. Graph shows bursting pressure of vessel.—INCO   17276

2.4.2
An Apparatus for the Photographing of an Evolute Surface of Cylindrical Metal Bodies for the Purpose of Carrying Out Corrosion Tests. (In Russian.) S. N. Alekseyev. Zavodskaya Lab., **24**, No. 1, 108-109 (1958).
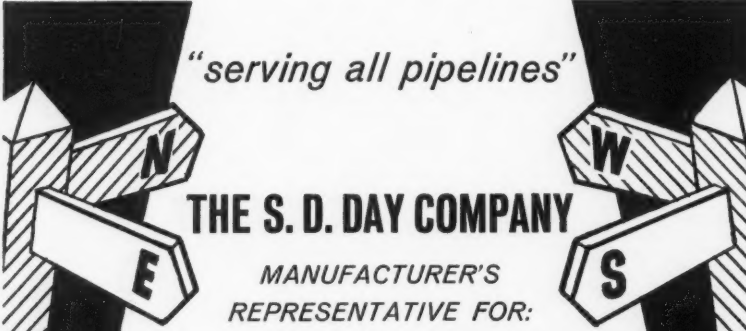
The principle of the apparatus described consists in taking a photographic picture of the surface of a cylindrical body through a narrow slit which corresponds to the length of the axis of this body; by causing the cylindrical body to resolve around its axis in front of the film camera a film is obtained that represents the unrolled surface of the cylindrical body. The same effect can be obtained if the film camera moves synchronically around the cylindrical body, but the first-mentioned order is technically more easily attained. The apparatus is sketched.—NSA.   17171

2.4.2, 6.2.2
Modified Keel-Block Design for Acceptance Testing of Ductile Iron. G. McGlothlin. Lynchburg Foundry Co. Iron Worker, **22**, No. 1, 30-32 (1957-58) Winter; Foundry Trade J., **105**, No. 2195, 563-566 (1958) Nov. 6.

Ductile iron requires more complex physical testing procedures than does grey iron, and as result, Lynchbury Foundry Co. developed an unconventional form of test-bar or block. Keel type test-block, used throughout steel

industry, was selected and modified. First modification employed 1 in. ASTM keel block dimensions, and by use of Washburn risering technique, parting notch was cast in the side of keel permitting either, or both legs to be knocked off with hammer blow. Second modification substituted 1 in. round legs for 1 in. square legs, thus providing more efficient shape for lathe and offering advantage of less stock to be removed in turning tensile specimen. Graph shows comparison of tensile strength and elongation for ASTM keelblock and Lynchburg modified keelblock.—INCO.   17469

2.5 Specifications and Standardization

2.5, 3.5.8, 6.2.5, 6.3.6

Material Rating Based Upon True Stress-Strain Properties. J. Martin and M. G. Sharma. Pennsylvania State Univ. Welding J., **37**, No. 8, 375s-378s (1958) August.

Gives results of study on material ratings based upon nominal and true mechanical properties in tension. Results show that these 2 ratings are not the same. Authors recommend that, in future, ratings be determined based upon true stress-strain relations. Table gives ratings of 56 materials based upon both nominal and true properties. Data are included for stainless steels, various nickel steels and copper-nickel. Graph shows log-log true stress-strain relation for Monel, copper, brass and bronze. Appendix gives derivation of true ultimate stress, true ductility and true toughness.—INCO.   17487

2.5, 5.6.1

Performance of Tests Required in Specification MIL-P-116C. S. Stambler. U. S. Naval Supply Research and Development Facility. March, 1957, 77 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 131332.)

Tests for conformance with a military specification for packaging materials and containers are outlined in this illustrated manual. Suggested test procedures, equipment required and performance of each test are described in detail. Tests are included for determination of cleanliness, determination of preservative compound application and preservative retention, leakage, cyclic exposure, hot seal and rough handling. Most of the steps in each test are illustrated with photographs.—OTS.   16321

3. CHARACTERISTIC CORROSION PHENOMENA

3.2 Forms

3.2.2, 4.7, 6.2.4

Cadmium Embrittlement of High Strength Steels at Elevated Temperatures. B. Cohen. U. S. Wright Air Development Center. Plating, **45**, No. 11, 1127-1132 (1958) Nov.

Experimental work to obtain quantitative data on embrittling effect of molten cadmium on stressed high strength steels. Typical aircraft high strength steels investigated were SAE 4340 (1.74 nickel) and SAE H-13 (1.53 nickel), and a chromium hot work tool steel known as Thermold J. Smooth and notched specimens of steel were tensile tested at room temperature, then elec-

troplated with cadmium, tensile tested in plated form at room temperature and then finally tested at 620 ± 10 F which is slightly abve melting point of cadmium. Room.temperature tests of plated specimens showed that no residual detrimental hydrogen embrittlement remained at test stress level. Cadmium drastically reduces tensile strength of the high strength steels when temperature exceeds melting point of cadmium. Embrittling effect of molten cadmium is instantaneous, resulting in extremely brittle type of failure. Embrittlement mechanism is proposed in 3 steps; stressed high strength steel deforms at grain boundaries, leading to higher concentration of dislocations; molten cadmium very rapidly diffuses into dislocated grain boundaries; and molten cadmium in grain boundaries interrupts continuity of structure and produces

hot shortness resulting in intergranular cracking of steel. Tables, photomicrographs.—INCO.   17215

3.2.2, 6.2.2, 3.5.8

Study of Hydrogen Embrittlement of Iron by Internal-Friction Methods. R. E. Maringer, E. B. Swetnam, L. L. Marsh and G. K. Manning. U. S. National Advisory Cttee. Aeronautics, Technical Note No. 4328, Sept., 1958, 62 pp.

Electrolytic charging, under the conditions adopted, produces severe structural damage in iron and in 4340 steel even after comparatively short charging times. Charge-induced damage appears, in part, to nucleate at internal flaws and grain boundaries. Internal friction of recrystallized iron is particularly sensitive to structural damage produced by hydrogen charging. Internal friction of

iron and steel below room temperature exhibits phenomena resulting from interaction of hydrogen atoms and moving dislocations. Much of the anomalous internal friction behavior observed in pure iron can be accounted for in terms of magneto-elastic energy losses. Graphs, photomicrographs.—INCO.   17485

3.2.2, 6.2.5, 3.4.6

Chloride Stress Corrosion Testing of Type 347 Stainless Steel Steam Generator Tubing. W. F. Brindley, L. R. Scharfstein and M. A. Golik, Bettis Tech. Rev., 1, No. 3, 1-22 (1957) Aug. U. S. Atomic Energy Commission Pubn., WAPD-BT-3.

Cracks in the stainless steel tubing varied in depth, averaging from 5-10 mils. Majority of cracks observed extended at least half-way around the circumference. Conditions of this test, particularly the considerable quantity of oxygen in the vapor, are extremely severe and are unlikely to occur in practice. However, they do serve to give comparative results on an accelerated basis. It appears that exposure to the vapor for an extended period of time was necessary to cause cracking. Inasmuch as vapor consisted of rather large amounts of oxygen it may be concluded that steam and oxygen are an important part of the mechanism leading to chloride stress corrosion cracking. Fact that cracking can occur in deformed tube in a crevice, with very little likelihood of chloride concentrating in a test of this nature, points to the important influence of the gaseous oxygen. Tables, photomicrographs.—INCO.   17023

3.2.2, 6.2.5, 4.3.3, 4.3.6

The Intercrystalline Corrosion of Stainless Steels. C. Edeleanu. Chem. and Ind., No. 42, 1360-1361 (1958) October 18.

Intercrystalline corrosion of austenitic steels is generally assumed to be the consequence of carbide precipitation in the steel and is successfully controlled either by heat treatment or, by stabilization of the steels with titanium or niobium. However, there are at least 3 cases in which intercrystalline failures are known to occur in steels which have been properly stabilized or in which the normal explanation cannot be applicable. One case is intercrystalline corrosion found in steel in caustic solutions at elevated temperatures. It seems that conditions leading to this type of failure can arise in plants using reasonably high purity waters provided that there is a heavy heat flux through the steel and the design is such as to allow concentration effects to occur. A second type of intercrystalline failure occurs with low carbon 18-8 molybdenum steel. It was found that what appears to be intercrystalline stress corrosion occurs in concentrated chloride solutions such as 42 percent magnesium chloride. Intercrystalline corrosion has also been found

with austenitic alloys in fused chloride. This type of cracking is again not believed to be the preferential leaching of the chromium by the salt. It appears therefore that there are at least 3 types of intercrystalline corrosion associated with the austenitic stainless steel which are not due to lack of stabilization and cannot therefore be avoided by merely ensuring that the steel is not susceptible to intercrystalline corrosion in the conventional copper sulfate nitric acid test. —INCO.   17252

3.3 Biological Effects

3.3.4, 4.5.3, 5.2.4
The Influence of Anaerobic Bacteria on the Current Density of Cathodically Protected Equipment in Soils. M. Solti and J. Horvath. Werkstoffe u. Korrosion, 9, No. 5, 283-291 (1958) May.

Usually applicable specifications for cathodic protection of buried steel pipes must be modified if anaerobic soil bacteria are present. Tests in soils containing high concentrations of sulfate reducing bacteria show that current density, deduced from initial polarization curve, does not guarantee sufficient protection. Increased protective effect was achieved in an inoculated culture medium when a more negative voltage was applied and maintained during 5 months duration of the experiment. Graphs. —INCO.   16647

3.3.4, 3.8.2
The Role of Micro-Organisms in Certain Corrosion Phenomena. (In French.) Lucien Baudon. Ind. chim. belge, 23, 983-990 (1958) Sept.

A brief survey is presented of the electro-chemical theory of corrosion. It is shown that the corrosion phenomena in which microorganisms play a role are connected to this theory. The different species of bacteria causing corrosion in ferrous and non-ferrous metals are described and their actions are interpreted. The means of protections against such biological corrosions are enumerated. (auth).—NSA.   17175

3.3.4, 6.3.8, 4.4.6, 4.4.2, 7.8
Micro-Organisms and Corrosion of Lead-Sheathed Cables. G. Bonde and Pörge Lunn. (In English.) Ingenioren—International Edition, No. 3, 103-107 (1958).

Among cable technicians the term phenol corrosion has been used for a corrosion of lead sheath following the paths of jute strings in the protecting cover. It has been assumed that this corrosion is due to a catalytical action from phenol present in the impregating materials. Later it has been found that microbial decomposition of the jute develops corrosion promoting organic acids, and the present authors have shown that a hydrocarbon decomposing bacterium, Pseudomanas Oleovorans, might promote corrosion of lead, especially when living on phenol-containing medium tar-oils and further this bacterium has been found in some cables which showed a typical picture of phenol corrosion.

By careful tests it has been shown that phenol cannot act as a catalyst for the corrosion of lead and even if phenol can attack when dissolved in simple hydrocarbons through a peroxide reaction, it is proposed that the previous assumption that phenol is a direct cause of corrosion is unjustied. It is much more probable that it is microbial decomposition products not only from the jute serving but also from the impregnating hydrocarbons which might attack the lead sheath.   17433

3.7 Metallurgical Effects

3.7.3
Fundamentals of Brazing for Elevated-Temperature Service. M. D. Bellware. Paper before Am. Welding Soc., Annual Spring Mtg., St. Louis, April 14-18, 1958. Welding J., 37, No. 7, 683-691 (1958) July.

Available information is reviewed and basic rules established to help fabricator obtain suitable brazed joints. Classifications of brazing considered are silver-base, copper-base, manganese-, gold-, and palladium-base. For service temperatures above 1000 F, nickel-base brazing alloys have produced best results. Nickel-base alloys contain elements that promote rapid interalloying, particularly at grain boundaries. Shot brazing times tend to reduce interalloying as well as liquation. With other brazing alloys mentioned, amount of alloying is usually slight. Proper cleaning prior to brazing is discussed, and inhibition of oxide formation during brazing by use of suitable atmosphere or flux is reviewed. When aluminum or titanium is present, it may be necessary to plate parts with nickel prior to brazing.—INCO.   17305

3.7.3
Welding Alloy Steels Under Bonded Fluxes. H. C. Campbell and W. C. Johnson. Paper before Am. Welding Soc., Annual Spring Mtg., St. Louis, April 14-18, 1958. Welding J., 37, No. 11, 1081-1085 (1958) Nov.

Bonded submerged-arc fluxes which are baked or matured at low tempera-

tures can be used in pipe welding, in preparing overlays or clad surfaces and in welding high-strength low alloy steels. Pipes down to 6 in diameter have been successfully welded with new bonded fluxes. Voltage, current, travel speed and height of flux burden have been evaluated for minimizing dilution yet still assuring adequate penetration in single-arc and series-arc overlay cladding with Types 308 and 309 filler metal. Progress has been made toward solving problem of welding Grade HY80 steel by submerged-arc welding using bonded fluxes incorporating alloying elements and active deoxidizers. Tensile data and Charpy V-notch impact test data down to —150 F are presented for HY80 welds. Tables.—INCO. 17287

3.7.3
High-Temperature Vacuum Brazing of Jet-Engine Materials. E. G. Huschke, Jr. and G. S. Hoppin, III. Paper before Am. Welding Soc., Annual Spring Mtg., St. Louis, April 14-18, 1958. Welding J., 37, No. 5, 233s-240s (1958) May.

Vacuum and some special hydrogen-brazing techniques for titanium and/or aluminum containing superalloys were studied. Pressure requirements for vacuum brazing selected alloys (A-286, Inconel 702, R-235, J-1570, 17-7 PH, U-500, J-1500, Inconel 700, Inconel X, Inconel W and J-1300) were determined. Pressures in range of 2-35 microns were found necessary for vacuum brazing of 3 representative alloys (A-286, Inconel 702 and R-235). Gas evolution per unit weight of A-286, Inconel 702 and J-1500 and of powdered filler materials (nickel-chromium-silicon and nickel-silicon-boron) was found to vary greatly with melting practice and weight/surface area. Results of sample calculations showing interrelationship between gas evolution during brazing and vacuum pumping capacity are presented. Strengths of vacuum and hydrogen brazed joints of easily brazed L-695 were found equal, while special techniques necessary to braze titanium- and aluminum-bearing R-235 in hydrogen resulted in lower joint strengths than were achieved in vacuum brazing. Titanium- and aluminum containing super alloys can be brazed in hydrogen by: plating surfaces to be brazed with iron or nickel; use of certain fluxes; preoxidizing and leaching of surfaces to be brazed; and preplacement of brazing alloy by flame spraying. Tables, graphs, photomicrographs.—INCO.
17113

3.7.3
A New Method of "Rivet Welding," Using Coated Electrodes. (In Russian.) A. Ya. Brodskyi. Svarochnoe Proizvodstvo, No. 10, 18-21 (1958); Engrs' Digest, 19, No. 11, 482-483 (1958) Nov.

To overcome disadvantages of original rivet-welding process, new and improved method, using coated electrode, has been developed in Russia, by means of which, when arc is struck, it begins to fuse hole in workpiece, thereby eliminating all drilling operations. Enclosed space is formed, bounded laterally by coating of electrode, above by electrode tip, and below by molten base of hole. Stream of incandescent ionized gases, evolved as electrode and coating melt, builds up pressure inside this space, and molten metal from workpiece and electrode flows around rim of coating and out over surface of workpiece. Ever-increasing depth of metal is exposed to direct fusing action of arc. Thick metal can be fused

or pierced very rapidly and with comparatively low currents. Details of method are shown schematically.— INCO. 17186

3.7.3
Inert-Gas-Shielded Arc Welding of Silicon and Aluminum Bronze. P. L. Hemmes. Revere Copper & Brass. Paper before Am. Welding Soc., Annual Spring Mtg., St. Louis, April 14-18, 1958. Welding J., 37, No. 8, 779-788 (1958) Aug.

Detailed information pertinent to proper joint design, welding procedures, shielding gas, operational techniques and mechanical strength of welded joints, using inert-gas-shielded metal-arc and inert-gas-shielded tungsten-arc processes. In addition to aluminum bronze welds and silicon bronze welds, data are given for dissimilar metal welds (aluminum bronze to steel, silicon bronze to steel, and aluminum bronze to silicon bronze). Silicon bronze contained 1 nickel. Tables, photomacrographs.—INCO. 17344

3.7.3, 3.7.4, 6.2.4
Effect of Cold Rolling and Heat Treating Conditions on Structure of Steel EI 428. (In Russian.) E. Yu. Chemadurova. Metalloved. I. Obrabotka Metallov., No. 10, 36-40 (1958) Oct. Translation available from: Henry Brutcher, Technical Translations, P. O. Box 157, Altadena, Calif.

Study of changes in structure of a 0.10 per cent carbon, 0.25 manganese, 1.60 silicon, 6.0 chromium, 0.85 aluminum, 0.015 phosphorus, 0.006 sulfur steel under various cold-working and heat-treating
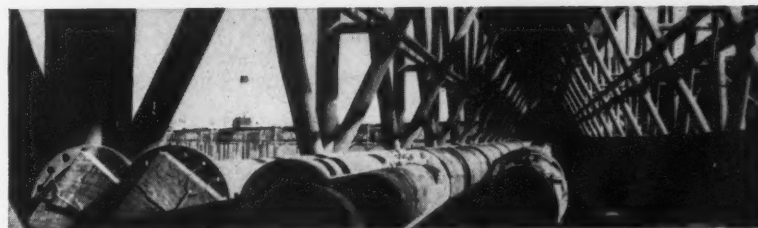
conditions to minimize its susceptibility to develop cracks in further processing (for example, into tubes). Results of X-ray and micrographic studies of effect of heat-treating practice upon structure. 2 figures.—HB.   17236

3.7.3, 6.3.20, 4.6.2
Corrosion Resistant Brazing Alloys for Zircaloy. Final Report (for) May 10, 1956 to July 9, 1957. Robert M. Necheles and Harry Schwartzbart. Illinois Inst. of Tech., Armour Research Foundation for Westinghouse Electric Corp. Atomic Power Division. U. S. Atomic Energy Commission Pubn., AECU-3836, July 25, 1957, 83 pp. Available from Office of Technical Services, Washington, D. C.

234a

More than 60 experimental alloys and a few commercial alloys were used to prepare brazements of simple design for exposure in an autoclave to 600 or 680 F water. Alloys studied include alloys of copper, aluminum, nickel and zirconium.—NSA.   16988

3.7.3
Metal Joining—Ultrasonic Techniques Used by Aeroprojects. P. Fossen. Missiles and Rockets, **4**, No. 24, 30, 32-33, 35 (1958) Dec. 15.

Reviews ultrasonic welding, brazing and soldering techniques and equipment developed by Aeroprojects Inc. Ultrasonic transducer couplings use both magnetostrictive nickel stacks and electrostrictive barium titanate as transducing materials. One of the most important advantages of ultrasonic welding is its ability to join dissimilar metals formerly considered impossible to weld together. Table listing metals and bi-metals successfully welded includes nickel, platinum, beryllium, Zircaloy, Kovar, among others.—INCO.   17266

3.7.3, 4.6.1
Joining of Zircaloy to Stainless Steel. J. B. McAndrew, R. Necheles and H. Schwartzbart. Illinois Inst. of Technology. Welding J., **37**, 529s-534s (1958) Dec.

The work reported was undertaken for the purpose of developing a zirconium-to-stainless-steel joint in heavy-wall tubing, the joint to incorporate a metalurgical seal which would not be attacked during long exposure to pressurized high-temperature water. Flash welding and brazing were the joining methods

investigated. Some weldments and brazements showed promise of meeting the requirements, but reproducibility of performance among different joints was poor in both cases. Thermally engendered stresses were a major source of difficulty, whereas it appears that the corrosion problem is not insoluble. (auth)—NSA.   17470

3.7.3, 4.7
Molten Metals and Alloys as Media for Heating Steel Articles During Heat-Treatment. (In Russian.) A. P. Garashchenko, A. P. Gulyaev and Z. S. Luneva. Metalloved. i Obrabotka Metallov, No. 1, 21-26 (1958).

Molten metals suitable for use as heat-treatment media should have low melting point and not dissolve iron. Lead, bismuth and magnesium satisfy these requirements. However, lead is scarce and toxic, bismuth expensive; magnesium and magnesium-aluminum give a high heating rate but are hazardous. Pure aluminum is unsuitable, as it dissolves iron. Plate specimens (30 mm diameter x 5 mm) of steels U8 and KhVG were heated for 10 min at 700, 800 and 850 C in the following molten aluminum alloys, then quenched (U8 in water, KhVG in oil): AL2O (silicon 8-10, iron 0.8, manganese 0.5, nickel 0.5, zinc 0.5 per cent), AL2O with iron (silicon 7.92-8.02, iron 6.4-10.47, copper 1, manganese 0.5, magnesium 0.4 per cent), AL2O with magnesium (silicon 9.02-9.92, magnesium 0.5-7.72, iron 1.12-1.47, copper 0-1 per cent). The weight loss and depth of attack were measured. The use of chalk powder or paste, oxide films (produced at 450-500 C), copper coatings and chromium plating, for protecting the steel from attack were investigated; chalk coatings were the best. The thermocouple sheath and iron crucible were protected with a mixture containing: ground chalk 62, waterglass 8, water 30 per cent. Aluminum alloy baths were also tested industrially; baths containing 8-12 per cent silicon were suitable for annealing, those containing silicon 6-10, iron 5-7 per cent for heating for quenching. Rates of heating were comparable with that for lead.—MA.   17341

3.7.3, 5.3.4
Seam Welding Galvanized Steel. W. J. Allen and M. L. Begeman. Welding J., **37**, No. 4, 138s-143s (1958).

In comparison with uncoated material higher currents and greater electrode forces are required to produce good nugget penetration in galvanized sheet. Continuous current is desirable but good welds can be obtained with a ratio of "on" to "off" time of 4.1. Lower ratios give bad arcing as the electrodes pull away solidified zinc. Considerable build-up of zinc on electrodes occurs, and continuous edge-width control is required. Well-penetrated welds have little zinc coating at the interface, but iron-rich iron-zinc alloy which has good corrosion-resistance. Excessive welding-heat causes the occurance of a brittle zinc-rich phase at the interface.—MA.   17322

3.8 Miscellaneous Principles

3.8.4
The Interaction of Oxygen with Clean Silicon Surfaces. J. T. Law. Physics Chem. Solids, **4**, No. 1/2, 91-100 (1958).

The oxidation kinetics on a vacuum-evaporated silicon film were measured by the rate of pressure change in a constant-volume system. With thin films, the

silicon particles, if spherical, have a diameter of 1150 A. A chemisorbed monolayer is rapidly formed. The slow oxygen uptake in the 1-2 monolayer region was investigated at 273-323 K; the rate $\propto$ the square root of the oxygen pressure; illumination does not affect the rate. All the data reported are for oxygen pressures of $10^{-1} - 4 \times 10^{-3}$ mm mercury. Evacuation experiments indicate that some type of re-arrangement of sorbed material is the slow step. 19 references.—MA. 17476

3.8.4, 2.1.1, 3.4.6, 6.3.9
The Kinetics of Interaction Between Gases and Metal Surfaces. (In Russian.) V. A. Arslambekov. J. Phys. Chem. (Zhur. Fiz. Khim.), 32, No. 1, 170-177 (1958).

A mathematical analysis of the process of interaction of gases and metal surfaces is followed by a practical study of the interaction of oxygen on molybdenum at 20 and 76 C. Equations are derived from which the energy of activation was calculated as 8.7 kcal/mole at 20 C, and 12.5 kcal/mole at 76 C.—MA. 17180

3.8.4, 2.3.6, 6.3.14
A Study of Natural and Artificial Oxide Films Formed on Pure Tin and Tinplate by Electron Diffraction and Electron Microscopy. (In French.) J. J. Trillat, (Mme) L. Tertian and S. C. Britton. Métaux-Corrosion-Industries, 32, No. 388, 475-481 (1957) Dec.

These films, formed in air at up to 218 C (natural films) and by immersion or electrolytically in potassium dichromate solution, chromium trioxide-phosphoric acid solution, and a proprietory solution (artificial films) were stripped and examined. The results indicate that the natural film formed at 218 C contains

stannous oxide. In the case of the film on tinplate there is in addition a second unidentified component, and for films formed below this temperature certain identification could not be made. In the artificial films, stannic oxide as well as stannous oxide and ferrous ferric oxide were identified. Electron miscroscopy confirmed the heterogeneity of the films, but gave no further information.—MA. 17081

3.8.4, 2.3.9
Application of Fe^{59} and Cr^{51} in the Investigation of Iron and Chromium Diffusion in Spinels NiCr$_2$O$_4$ and NiAl$_2$O$_4$. (In Russian.) I. N. Belokurova and D. V. Ignatov. Atomnaya Energiya, 4, 301-302 (1958) March.

The diffusion parameters of chromium and iron in the oxides NiCr$_2$O$_4$ and NiAl$_2$O$_4$ were determined and correlated with the oxidation rate of the alloys. The temperature dependence of the diffusion coefficients are presented graphically.—NSA. 17184

3.8.4, 2.3.9
The Study of Freshly Deformed Metal Surfaces with the Aid of Exo-Electron Emission. L. Grunberg. Wear, 1, No. 2, 142-154 (1957).

Deformed metal surfaces produce counts in point-counters, counting tubes and electron multipliers, and the emission was first ascribed to latent heat developed in phase changes or in reaction with oxygen. Now it is known that surface films on deformed metals contain special electronic energy levels associated with imperfections in the oxide lattice, which can be excited thermally or optically. The decay of emission depends on the atmosphere with which the surface is in contact. 19 references.—MA. 17018

3.8.4, 2.3.9, 6.3.10
Ion Induced Reemission of Noble Gases from a Nickel Surface. J. H. Carmichael and E. A. Trendelenburg. Westinghouse Res. Lab. J. Applied Phys., 29, No. 11, 1570-1577 (1958) Nov.

Each of noble gases, helium, neon, argon and krypton, has been ionically pumped with energy of about 100 ev into nickel target and subsequently released by similar bombardment using different noble gas. Mass spectrometer measured both reemission of trapped atoms and trapping of bombarding particles. Reemission mechanism is described in terms of simple model which assumes that trapped atoms are released by bombarding particles through mechanism of sputtering of either nickel target or trapped gas or combination of both. Experimental results agree with model. Direct replacement of trapped atom from its trapping site by bombarding particle is relatively unimportant factor in reemission process. Measurements of reemission rates of trapped atoms yielded information concerning depth distribution of trapped atoms in nickel target. Graphs.—INCO. 17151

3.8.4, 3.2.2, 3.7.2, 3.8.3, 5.2.1
Corrosion Mechanisms and Materials Selection Methods. F. L. IaQue. Paper before Am. Inst. Chem. Engrs., Golden Jubilee Mtg., Philadelphia, June, 1958. Chem. Eng. Progress, 54, No. 11, 58-64 (1958) Nov.

Discussion of factors that determine rates of corrosion reactions and mechanics of reactions themselves. Passivity, potential pH relationships, cathodic protection and pitting are considered. Causes of stress corrosion cracking of steel are given and effects of nickel are described.

When susceptibility to cracking in alloys that contain 18 chromium is related to nickel content of alloy, it is observed that maximum susceptibility occurs with a nickel content around 8% and then decreases rapidly so that it is very low when the nickel content is around 40% and disappears entirely at the 75 nickel level in the alloy Inconel. The possible reasons for this behavior are given. Process plant tests are discussed as to hot and cold wall effects, effects of corrosion products, velocity :ffects and effects of surface condition, stress and heat treatment. 37 references.—INCO. 17471

3.8.4, 3.4.6
Electron Emission from Evaporated Metal Films. J. Wüstenhagen. Naturwiss., **44**, No. 7, 228-229 (1957).

Freshly prepared metal surfaces (e.g. by scraping) exhibit an electron emission which is dependent on the oxygen pressure. To clarify the processes involved, a comparative study was made of emission from freshly evaporated metal surfaces. The rate of decrease of emission intensity with time was measured for aluminum films approximately 100 A thick at different oxygen pressures. The intensity decreased with time or decreasing oxygen pressure in a similar manner to that from a scraped surface. It is concluded that mechanical deformation is not a necessary condition for emission, which instead must be associated with interaction of the metal surface and oxygen. In confirmation, it was established for both aluminum and beryllium that no measurable renewal of emission took place on admitting an inert gas (nitrogen) in place of oxygen. Further, the complete and rapid evacuation of oxygen stopped the emission, which recommenced only on re-admitting the gas.—MA.   17079

3.8.4, 3.4.6
The Reaction of Oxygen With Lead Selenide. R. H. Jones. Proc. Phys. Soc., **70**, Section B, No. 11, 1025-1032 (1957).

A powdered sample of a p-type lead selenide single crystal was oxidized at 19-280 C. Oxidation was initially rapid, indicating diffusion of oxygen ions to vacant selenium sites with an activation energy of 17 kcal/mole. Subsequently oxidation was slower, diffusion being more difficult once the vacant selenium sites had been filled. Calculations based on the amount of oxygen absorbed at the end of the rapid stage indicated that 1 in 57 selenium lattice sites was vacant. These observations support earlier electrical measurements on lead selenide films exposed to oxygen.—MA.   17004

5. PREVENTIVE MEASURES

5.3 Metallic Coatings

5.3.4
The Tensile Strength of Solid-State Bonded Aluminum and Nickel-Plated Uranium. H. A. Saller, R. F. Dickerson and R. J. Carlson. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-956, October 21, 1954 (Declassified Feb. 13, 1957), 24 pp. Available from Office of Technical Services, Washington, D. C.

To aid in the evaluation of solid-state bonding techniques for cladding natural-uranium fuel-element cores with aluminum, tensile specimens, ¼ in. in diameter and 3 in. long were made and tested. Results show that these techniques are capable of producing satisfactory bonds

between aluminum and nickel-plated uranium. Pressing conditions of 1 min at 950 F and 6000 psi produced consistent bond strengths equal to the yield strength of 2S aluminum. When optimum bonding conditions are used, anodic activation and strike-current density are not critical to bond strength. Nickel plating of the aluminum component of the bond couple reduced the tensile strength by about 50%. (auth)—NSA.   16323

5.3.4
Application of Precoated Steel Sheets in Industry. F. H. Smith. Sheet Metal Ind., **34**, No. 368, 915-923, 928 (1957).

Potential advantages of various precoating treatments (hot dipping, electrodeposition, cladding) from the point of view of cost and surface finish, jointing, storage, pressing, painting of precoated sheet and service tests on car bodies made from precoated sheet are described. —RPI.   16292

5.7 Treatment of Medium

5.7.3, 3.4.6, 4.6.2, 7.6.4
Hydrazine Assures Effective Deaeration. J. R. Coursault. Betz. Labs. Power Eng., **62**, No. 12, 84-85 (1958) Dec.

Deaerating heaters in common usage

for removal of noncondensable gases from boiler feedwater can reduce dissolved oxygen to a low level. Nevertheless, industrial plants and utilities normally find the use of a chemical deaerant advisable to minimize difficulties with oxygen and pitting from residual oxygen present in boiler feedwater. While sodium sulfite has served effectively for this purpose difficulties have been experienced from acidic decomposition of sulfite at high pressures. Unlike sulfite, hydrazine will dissociate to form an alkaline material. Since the breakdown of hydrazine occurs at high pressures, use of hydrazine is particularly attractive to utilities and industrial plants with boilers operating above 600 psi. With hydrazine, chemical deaeration is achieved without the addition of any solids to the boiler water since hydrazine will react with oxygen. Graphs.—INCO.   17225

5.7.7, 6.4.2, 8.4.5
Optimum pH for PFTR Coolant and Moderator with Aluminum Process Tubes. R. B. Richman and R. J. Lobsinger. General Electric Co., Hanford Atomic Products Operation. U. S. Atomic Energy Commission Pubn., HW-53672, Sept. 23, 1957, 5 pp. Available from Office of Technical Services, Washington, D. C.

The most desirable operating conditions resulting in minimum corrosion of aluminum shroud tube and calandria surfaces without undue sacrifice of process tube life appear to be adjustment of coolant and moderator pH to approximately 6 and operation with coolant temperature not greater than 183 C.

Coolant and moderator pH of 6 is desirable because the demineralizers contemplated for use with the PFTR provide water at this pH.—NSA.   17057

5.11 Design-Influence on Corrosion

5.11, 7.9
Coiled Stainless Steel Tubing: Part 2. Design Manual. R. D. Stouffer, J. T. Hudson and L. F. Freitag. The Martin Co. for U. S. Wright Air Development Center. Dec., 1957, 45 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C. (Order PB 131720).

This manual is intended to assist and instruct designers in using plain metal tubing to solve problems requiring flexibility or relative motion in plumbing for aircraft hydraulic and pneumatic systems. Two series of standard configurations of tubing which provide great flexibility are presented along with instructions and limitations for their application or installation. The volume also covers variations from the standards, using simple elements to build up any configuration necessitated by particular installation requirements. Analytical procedures for evaluating any configuration with respect to structural limitations are also presented.—OTS.   16277

5.11, 8.8.5
Designing with Permanent Magnet Materials. R. P. Smith. General Electric Co. Materials in Design Eng., **46**, No. 3, 126-128 (1957) Sept.

Difficulties in fabricating hard, brittle Alnico-type materials are alleviated by proper design. Helpful suggestions are presented on: insert design for cast and sintered magnets; soldering, welding and bonding; building up surfaces by sleeves and enclosures, metal spraying or die casting; and finishing surface with paint, plating, nylon, plastic or Celastic.—INCO.   16332

5.12 Metallurgical Treatment

5.12, 6.2.2, 3.7.3, 8.10.2
Heat-Treated Powder-Iron Parts for Improved Strength and Hardness. N. Kothari. Dixon Sintaloy Inc. Machine Design, **30**, No. 22, 93-96 (1958) October 20.

Properties of ferrous parts produced by powder-metal process can be improved by same conventional heat-treatment techniques used on plain-carbon and low-alloy steels. Results of studies on effects of heat treating indicate that it is now feasible to heat-treat powder-metal parts on production basis. Metallurgical aspects are complex, and influence of certain factors of composition on end properties must be considered prior to heat treating. Data presented show how such factors as density, porosity and type of iron powder, affect mechanical properties when parts are subjected to: carburizing, carbonitriding, carboaustenitizing. Test specimens were made from: iron, iron-graphite, and iron-copper-graphite. Tables, graphs.—INCO.   17455

5.12, 6.2.5, 3.7.3, 3.5.8
Stress Relieving of Stainless Steels and the Associated Metallurgy. R. A. Huseby. A. O. Smith Corp. Welding J., **37**, No. 7, 304s-314s (1958) July.

Welding Research Council interpretive report covers major classifications

of stainless steels—martensitic, ferritic and austenitic. Residual stresses induced by fabrication operations of austenitic stainless steels may drastically affect behavior in certain corrosive environments (stress corrosion) and dimensional stability. Heating to conventional range of temperature for stress relieving is within temperature range that affects microstructure and may result in diminishing ductility, impact properties and general corrosion resistance. Stress relieving of austenitic stainless steels is employed only for conditions where severe stress corrosion may be encountered. Thermal stress relieving of ferritic stainless steels after fabrication is necessary to obtain desired mechanical properties and corrosion resistance. Martensitic stainless steels require preheating and high interpass temperatures during welding and immediate post-heating after welding to avoid cracking. Postheating temperature usually is temperature required for stress relieving. Tables, graphs, photomicrographs.—INCO.   17103

6. MATERIALS OF CONSTRUCTION

6.7 Duplex Materials

6.7.2, 2.3.7

Evaluation of Tensile, Compressive, Torsional, Transverse and Impact Tests and Correlation of Results for Brittle Cermets. Research Paper No. 2895. M. J. Kerper, L. E. Mong, M. B. Stiefel and S. F. Holley. J. Research Nat. Bur. Standards, **61**, No. 3, 149-169 (1958) Sept.

Static tests were studied for determination of mechanical properties of brittle cermets of 5 different compositions: 6 cobalt-94 tungsten carbide, 13 cobalt-87 tungsten carbide, 30 nickel-70 titanium carbide, 70 chromium-30 alumina, and <10 boron->90 zirconium boride. Designs of specimens and apparatus, suitability of tests to materials, refinements in test procedures, variability of results and their correlation were studied. Elastic properties were obtained from tensile, compressive transverse tests and modulus of rigidity calculated from results of these tests agreed with that from torsional test. Tensile strength was obtained from tensile, torsional and transverse tests on specimens of comparable sizes in accordance with limiting tensile strain. Shear strengths were obtained in compression tests. Correlation of impact values with mechanical properties was unsatisfactory. Tables, graphs, 43 references.—INCO.   17357

6.7.2, 7.1

A Study of Graded Cermet Components for High-Temperature Turbine Applications. H. W. Lawendel and C. G. Goetzel. Sintercast Corp. of America for Wright Air Development Center, U. S. Air Force, August, 1957, 47 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. (Order PB 131434).

Describes a preliminary study of graded cermet components designed to improve ductility and toughness of the root and airfoil tip sections of jet aircraft turbines. Ballistic impact tests were performed on a wedge-like simulated turbine bucket shape divided into areas representing root, airfoil tip, and airfoil body sections. A cermet of titanium carbide infiltrated with molten Inconel-X

was used for the core of the bodies. Used for the metal-rich layers applied to the root and airfoil sections was an alloy of Inconel-X enriched with titanium carbide. A structure was obtained in which the graded surface layer constituted a continuation and extension of the nickel alloy matrix of the cermet core containing dispersed titanium carbide inclusions. Substantial improvement in ballistic impact strength was shown to be gained by providing metal-enriched areas at the edges and tip of the airfoil. Cladding the entire component with an oxidation-resistant ductile alloy layer improved the thermal shock resistance of the titanium carbide bodies.—OTS.   17011

7. EQUIPMENT

7.2 Valves, Pipes and Meters

7.2, 5.4.5, 1.2.2

Lightweight Pipe with a Thin Film for Gathering Lines. J. N. Hunter, Jr. Service Pipe Line Co. Oil & Gas J., **55**, No. 37, 130-132 (1957) Sept. 10.

It is now possible to realize savings in both investment and operating costs by using lightweight pipe with a modern thin-film coating on gathering lines. Performances of various synthetic resin coatings are discussed. Shortcomings are high cost and carefully controlled conditions required during application to get a uniform film with desired properties. Manufacturers are marketing a special irrigation pipe which is coated where it is rolled and still others are considering coatings which can be mill applied and stand rough handling. Photos, graph, table.—INCO.   15855

7.2, 6.3.10, 5.11, 3.5.9

General Design Considerations for Smaller Gas Turbines. W. T. Von Der Nuell. Paper before Am. Soc. Mechanical Engrs., Fall Mtg., Hartford, Sept. 23-25, 1957, Trans. ASME, **80**, No. 4, 941-957; disc. 957-958 (1958) May.

Future of smaller gas turbine depends at least as much on development of better materials as that of big units and possibly even more so in that cost of materials and simpler ways of shaping them may be a more critical issue when smaller units become a mass-produced item for industrial and automotive power. For components of turbine proper, structural materials of high strength at high temperature with satisfactory resistance against scaling and corrosion and best possible ductility are required. Wrought nickel base alloys, Inconel X and Nimonic, are widely used for blades and wheels. Alloys such as 19-9DL, 19-9DX, 18-8 are well proved and suited for normally stressed hot wheels. Among more recent nickel base alloys, Inconel 700 is considered strong and useful up to 1650 F. Inconel 713C is a nickel-chromium cast alloy with strength up to 1700 F, good resistance to thermal fatigue and is considered attractive for gas-turbine blades. In sheet form, materials such as Inconel 702 and Incoloy 901 are fairly well known. Inconel 702 appears to have a particularly good oxidation resistance and in tests conducted between temperatures of 2000-2400 F, Inconel 702 was better in oxidation resistance than Inconel which, in turn, is superior to Inconel X. Vacuum-melted alloys display marked

superiority with respect to elevated-temperature strength and ductility over corresponding air-melted material. Alloys tested to allow for a comparison of mechanical properties in range 1000-1600 F include J-1570, Waspaloy, L-605, S-816, 19-9DX, GMR-235, N-155. Alloy R-235 is produced by vacuum melting, and is a nickel base, aluminum and titanium containing alloy with good properties up to 1750 F. Graphs, diagrams, photos, 69 references.—INCO.

16362

7.6 Unit Process Equipment

7.6.5, 3.5.4, 8.4.5

Development of a Waste Calciner. Progress Report on Waste Processing Development Project. B. Manowitz and S. Swickler. Brookhaven National Lab. U. S. Atomic Energy Commission Pubn., BNL-447, April, 1957, 11 pp. Available from Office of Technical Services, Washington, D. C.

The work of the Waste Processing Development Project at Brookhaven National Lab. has led to the development of a piece of equipment capable of substantially reducing the volume of high activity aqueous waste streams. This equipment, known as a "continuous calciner," is a heated-tube auger-agitated concentrator which dehydrates and fuses the various aqueous salt solutions to an anhydrous free-flowing melt on a continuous basis. A pilot plant model of this equipment has been operated successfully with an attendant decontamination factor of approximately 1000. The corrosion rate of mild steel in neutralized solutions and in the fused salt product was studied. No corrosive effects were detected, which indicated that mild steel is a safe storage container material. An economic evaluation was also made to compare relative costs of processing and storing an acid waste solution in a raw, neutralized, or anhydrous state. (auth).—NSA.

15979

Packed Fractionating Columns. S. R. M. Ellis and J. Varjavandi. Chem. and Process Eng., **39**, No. 7, 239-243 (1958) July.

Gauze packings posses a rather high fractionating efficiency due to the large active surface area per unit volume. They do not suffer from loss of efficiency at higher reflux rates since structure of packing ensures that active surface area remains constant up to flooding. Gauze trays made of 40 mesh nickel wire used for vapor liquid contacting are discussed. Stedman packings are generally made of stainless steel wire cloth which has been embossed and trimmed into flat, truncated, conical discs. Goodloe packing is made of 0.0045 in. diam. Monel wires with 12 filaments, twisted together to form a strand. Photos, graphs, 43 references.—INCO. 16973

7.7 Electrical, Telephone and Radio

7.7, 5.9.4, 5.4.5

Anodized Aluminum Conductors. J. Prieux. Schweiz. Archiv., **23**, No. 6, 202-208 (1957).

The preparation, properties and applications of anodized aluminum electrical conductors are reviewed. It is common practice to impregnate the anodized film with an epoxy resin coating.—RPI.

16264

7.7

Improving Performance of Silver-Zinc Batteries. P. L. Howard. Electronic Inds., **17**, No. 1, 61-63 (1958) July.

In 8 short years, the silver-zinc battery has evolved from a laboratory unit with simple cellophane separators and powdered electrodes to a sophisticated item. It is used in missiles, rockets, aircraft, torpedoes, portable power sources and radio control applications. Foremost is its output per unit of weight and space—up to 6 times greater than that of lead acid or nickel-cadmium couples. Silver-zinc batteries can supply 5 to 6 times more power than standard batteries of equal size. Battery cases and covers cast from HK 31, a new magnesium alloy containing thorium and zirconium, have been introduced. Used with batteries employed in Bomarc IM-99 interceptor missile, this rugged alloy proved to be even better than stainless steel in its ability to withstand severe shock and vibration requirements. Diagrams, photos.—INCO.

16873

ALLIED CHEMICAL'S HOTLINE ENAMEL SOLVES HOT-SIDE PROBLEMS

Allied Chemical's Hotline Enamel takes high temperature punishment from the hot-side of compressor stations . . . for years! Allied Chemical's Hotline Enamel won't crack at −10°F.—as proved in laboratory tests and on-the-job performance for leading public utility companies.

Allied Chemical's *Job-Matched* Hotline Enamel is derived from coal-tar pitch, thus possessing inherent protective properties against the damaging effects of water, soil chemicals and electrical currents. In addition to these properties, Hotline Enamel is bargain rated both for initial cost and long-run service.

Provides improved protection under all these specific conditions:

1. Hot gas pipelines, on discharge side of compressor stations where line temperature is above 120°F.

2. On pipe-type cables or "oil-o-static lines" which are subject to internal electrical heat from high-voltage surges.

3. Warm, swampy areas or other places where excessive soil stress on pipelines is encountered.

4. Areas where backfill and trenches are rough, rocky or contain foreign objects which normally penetrate softer coatings.

5. Pipelines (such as heated fuel lines) where temperatures are consistently high most of the time. but do not exceed 180°F. or for short-term exposure, 200°F.

A staff of Field Service Experts are at your call to offer you technical assistance that can save you maintenance time and costs.

PLASTICS AND COAL CHEMICALS DIVISION
40 Rector Street, New York 6, N. Y.

Allied Chemical

INDEX TO ADVERTISERS

8. INDUSTRIES

8.1 Group 1

8.1.2, 6.2.5

A Mile of Roof Drainage in Stainless Steel. L. E. Gichner. Heating and Air Conditioning Contractor, **49,** No. 9, 68-71 (1958) June.

New roof drainage system on Washington's Internal Revenue building is made entirely of stainless steel. Use of stainless steel for roof trim points up trend toward this metal on all types of architecture, modern and traditional. In addition to its excellent corrosion resistance, stainless offers the contractor and the architect high tensile strength, beauty and maintenance-free service. But it requires a greater degree of accuracy in layout work and greater care in fabrication than most of the sheet metals traditionally used in buildings. Photos.—INCO.   16531

8.1.3, 5.2.3, 7.6.5

Cathodic Protection in Industrial Refrigerating Plant. L. Piatti and H. Bourquin. Sulzer Technische Rundschau, **39,** No. 4, 31-37 (1957); Engrs' Digest, **19,** No. 2, 59-60 (1958) Feb.

Present practice at Sulzer is to employ cathodic protection for evaporators of ammonia refrigerating plant. Initially, sacrificial anodes were used but results were not satisfactory. Protection by ex-

ternal current is now used. Typical case where external current has given required protection is cited. Ice generator in brewery consists of steel tank with centrally arranged ammonia-type vertical-tube evaporator, ice cans on both sides passing through deep-freeze sodium chloride brine. Graphite anodes could only be fitted in the 4 corners of the tank. Using rectifier with considerable amount of current, it was not possible to reduce potential of sheet-metal walls of tank to value below —0.85 V. Cathodic protection was restricted to evaporator system itself, and using total current of only 9 A, protective potential reached permanent value not exceeding —1.4 V. Selection of suitable coating to use in conjunction with cathodic protection is discussed.—INCO.   15891

8.3 Group 3

8.3.1, 4.3.4

Corrosion of Metals by Liquid Mixed Fertilizers. J. D. Hatfield, A. V. Slack, G. L. Crow and H. B. Shaffer, Jr. J. Agricultural and Food Chem., **6,** 524-531 (1958) July.

Both mild steel and stainless steel were satisfactorily resistant with practically all combinations of variables tested. Aluminum resistivity ranged from unsatisfactory to satisfactory.— BTR.   16502

8.3.3

Plated Finishes—The Choice Widens. R. T. Gore and R. M. MacIntosh. Product Eng., **28,** No. 17, 81-84 (1957) October 28.

Reference chart of properties and applications of alloy and single-metal electroplates covers: base metals, uses, thickness, corrosion resistance, finish, adhesion, hardness, abrasion resistance, ductility, solderability and reflectivity. Plating materials listed are: bronze, tin-cadmium, tin-palladium, tin-nickel, tin-zinc, brass, white brass, cadmium, chromium, copper, gold, lead, nickel, rhodium, silver, tin and zinc.—INCO.   16200

8.9 Group 9

8.9.1, 6.3.15, 8.8.5

Hot-Sizing Titanium and High-Temperature Steel Parts. C. O. Herb. Machinery, **64,** No. 10, 118-121 (1958) June.

In manufacture of supersonic planes and faster projected missiles, principal problem has been fabrication of components from titanium and high-temperature resistant steels. Many parts of great variety must be formed from sheets of these materials. With work of this category, difficulties arise in producing the parts accurately to specified dimensions and to required shapes. North American aircraft company engineers developed a more satisfactory method of solving this problem. Their efforts led to the building of several proto-type hot-sizing presses on which patent applications are pending. Workpieces handled by these hot-sizing presses are as heavy as 0.093 inch in thickness and as light as only 0.005 inch. Parts are hot-sized in less than 3% of the time formerly required with bench work and are far more accurate. Photos.—INCO.   16919

8.9.5, 3.7.3
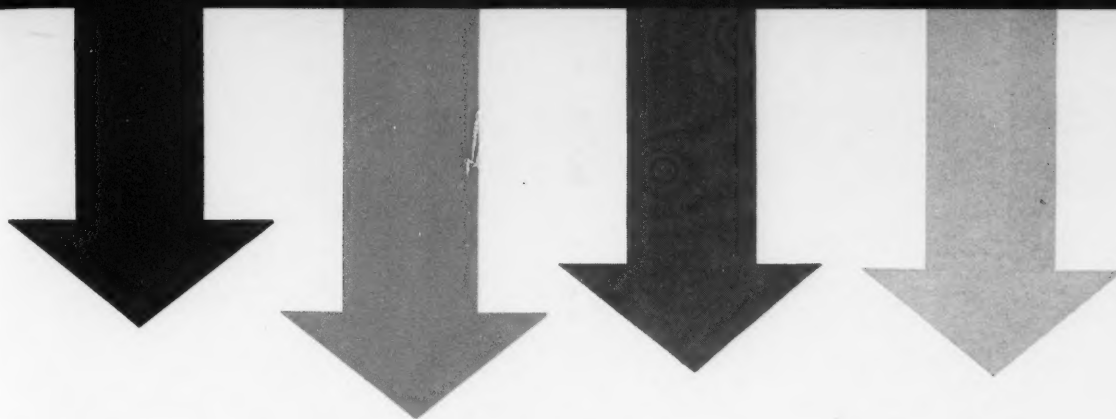
First Manned U. S. Spacecraft: X-15 Design Details. I. Stambler. Aviation Age, **30,** No. 1, 22-23, 144-148 (1958) July.

Detailed description of the X-15 covers design, materials, fabrication and testing. For its baptism of fire on reentry, X-15 will wear complete external armor of Inconel X. Most of bulkheads are of A110 titanium. Precipitation hardening stainless steels AM350 and AM355 are used for some of parts requiring severe forming. Some aluminum is used internally where high heat and high loads are not a problem. 65% of plane's structure is welded. Temperature will range down from about 1000 F maximum to —300F in some areas (temperature of its liquid oxygen fuel). Wing skins are made by machine-fusion welding 3 sheets of Inconel together. Main spars are made by welding corrugated webs of Inconel to spar caps. Other stiffeners are riveted to skins with Monel rivets.—INCO. 16843

8.9.5, 6.2.2

Recent Metallurgical Problems in Marine Engineering. B. Tood. Trans. Inst. Marine Engrs., **69,** 320-325 (1957) Aug.

Examples of corrosion of condenser tubes, propeller shaft liners, ships' side valves of spheroidal graphite iron; brittle fracture of wrought iron anchor cables; fatigue failure of diesel engine pistons of spheroidal graphite iron; causes and preventives. 11 references. —MR.   16378